OXIDATIONS OF SOME NON METALS IN ACETONITRILE.

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for the degree of M.Sc.

BY

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In memory of my father James Gerard McGhee

(1923 - 1987)

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SUMMARY

The oxidation of some non-metals in acetonitrile is described in this thesis. The iodine cation $I(NCMe)_2^+$ is linear and centrosymmetric and iodine EXAFS data show the I-N bond distances to be similar in the solid 2.17 Å and in MeCN solution 2.14 Å. Bond distances were determined for $[I(py)_2][NO_3]$ and $[I(py)_2][MoF_6]$ for comparison purposes. Molybdenum EXAFS data were used to determine the Mo-F distance in the MoF_6^- anion. The three compounds studied were $[I(py)_2][MoF_6]$ in MeCN 1.77 Å, $[I(NCMe)_2][MoF_6]$ in MeCN 1.77 Å, and $[Ag(py)_4][MoF_6]$ solid 1.79 Å. The MoF_6^- anion bond length had previously been determined by powder diffraction and was found to be 1.74 Å.

The oxidation of bromine in MeCN by UF_6 gives the salt $[Br(C_6H_9N_3)][UF_6]$ but no reaction occurs between Br_2 and MoF_6 in MeCN; this provides the first chemical reaction which differentiates between the oxidising abilities of these two hexafluorides. The cation $Br(C_6H_9N_3)^+$ oxidises NO gas to NO^+, I_2 to I^+ and the solvated Cu^I cation to the solvated Cu^{II} cation. No simple $[Cl(NCMe)_x]^+$ cations are obtained using the conditions adopted in this study; UF_6 is reduced to UF_5NCMe in the presence of Cl_2 in MeCN and substitution takes place to give $UF_{5-x}Cl_xNCMe$ species in solution. Similar reactions occur between HCl and UF_6 in MeCN.

Tellurium is oxidised in MeCN by MF_6 where M = Mo or U, to give $[TeF_3(NCMe)_2][MF_6].3MF_5NCMe$. Although SbF_5 and AsF_5 are strong oxidising agents in acidic media, the complexes $SbF_5.NCMe$ and $AsF_5.NCMe$ are weak oxidising agents in MeCN. Oxidation of tellurium by these species is limited to the formation of Te_4^{2+},

whereas oxidising agents MoF_6 and UF_6 oxidise the tellurium through to Te^{IV}. The NO^+ cation shows intermediate oxidising behaviour and WF_6 does not oxidise tellurium in MeCN.

The order of oxidising ability established experimentally is $UF_6 > MoF_6 > NO^+ > SbF_5NCMe$, $AsF_5.NCMe > WF_6$.

The brominating ability of $Br(C_6H_9N_3)^+$ was studied using several aromatic compounds. Two other sources of electrophilic bromine were prepared, Nafion-Br and $[Br_3][SbF_6]$; these were used to compare the brominating capabilities of the $Br(C_6H_9N_3)^+$ cation. $[Br(C_6H_9N_3)][UF_6]$ brominates, toluene, anisole, 9-methylanthracene, 4-s-butylphenol, benzaldehyde and nicotinic acid. It does not brominate phthalic anhydride or pentafluorobenzene. The salt $[Br_3][SbF_6]$ brominates 4-s-butylphenol, nicotinic acid and benzaldehyde. This salt reacts exothermically with the organic compounds studied in this work and causes fragmentation of the organic molecules. The halogenating powers of Nafion derivatives were studied. Nafion-Br proved to be a poor brominating agent, due to the slow release of the active "Br^+" species. Nafion-Cl was found to behave similarly.

CHAPTER ONE

INTRODUCTION

AIMS OF THE WORK

The aim of this project was to oxidise p-block elements to form new cationic species and to study the redox and solution chemistry of the resulting cations. The $I(NCMe)_2^+$ cation was the starting point for the work, and the synthetic methods used throughout, were similar to those used in the preparation of the iodine (I) salts. By generating "positive" non-metallic species, it was hoped that electrophilic reagents could be obtained which may have use in organic synthesis. Bromine was the first element to be investigated, this was followed by chlorine, which proved more difficult to oxidise. Tellurium was chosen as an example of a Group VI element. Polynuclear cations are formed when non-metals are oxidised in acidic media.[1] By using the basic solvent acetonitrile, it was hoped that monoatomic cations could be formed by analogy with oxidations of metallic elements, a topic which has been extensively investigated in this Department.

1.1 Homopolyatomic Cation Formation in Acidic Media.

Group VII Cations :

There are many compounds in which chlorine, bromine and iodine are found in the +1 oxidation state. This has led to the assumption that cations such as Cl^+, Br^+ and I^+ are important as stable entities or at least are plausible intermediates.[2] No evidence exists however for monoatomic Cl^+, Br^+ and I^+ as stable species.[1,3] In contrast, whole series of polyatomic halogen cations are known.

It is found that for groups at the extreme ends of the Periodic Table, ionisation energy decreases with increasing atomic size of the element.[4] No fluorine cations have been prepared, and the ease of cation formation increases down the group. Just over fifty years ago Masson postulated the existence of the cations I_3^+ and I_5^+ in solutions of iodine and iodic acid in sulphuric acid. He used these cations to explain the stoichiometry of the reaction of such solutions with chlorobenzene to form iodo and iodoso derivatives.[5] It was thought that the blue solutions obtained from dissolving iodine in strongly acidic media were due to the formation of I^+.[6] This was incorrect and it has been shown by conductimetric, spectrophotometric and magnetic susceptibility measurements for example, in fluorosulphuric acid that the species responsible for the blue colour is the I_2^+ cation.[7,8,9] Single crystals of $I_2Sb_2F_{11}$ have been prepared by reacting I_2 and SbF_5 in SO_2.[10] An X-ray crystallographic study shows the presence of discrete I_2^+ cations with $Sb_2F_{11}^-$ anions.[11] The cation I_3^+ has been shown to exist in acidic media by conductimetric and cryoscopic measurements.[12] When I_2 is dissolved in a solution of I_3^+ in 100% H_2SO_4 the absorption spectrum of the solution changes

but there is no change in the conductivity or freezing point of the solution. It is concluded from this evidence that I_5^+ and possibly I_7^+ are formed.

Bromine Cations.

Oxidation of bromine with an increasing amount of peroxydisulfuryl difluoride ($S_2O_6F_2$) in solution in fluorosulphuric acid (HSO_3F) gives rise to the successive formation of Br_3^+, $BrOSO_2F$ and $Br(OSO_2F)_3$.[13] The cation Br_3^+ is however not completely stable in this medium and $Br_3^+SO_3F^-$ is approximately 50% disproportionated in a dilute solution according to the equation:

$$4Br_3^+SO_3F^- = 4Br_2 + 4BrOSO_2F \qquad (1)$$

When bromine and $S_2O_6F_2$ are added to the superacid system SbF_5-$3SO_3$-HSO_3F further oxidation occurs giving Br_3^+, Br_2^+, $BrOSO_2F$ and $Br(OSO_2F)_3$. In this medium the Br_3^+ ion appears to be stable but the Br_2^+ ion is considerably disproportionated to Br_3^+, $BrOSO_2F$ and $Br(OSO_2F)_3$.[13] The Br_2^+ cation in superacid has a characteristic cherry red colour λ_{max} 510 nm, and a single Raman band at 360 cm^{-1}. The paramagnetic crystalline compound $Br_2^+Sb_3F_{16}^-$ has been prepared[14,15] by the following reaction:

$$9Br_2 + 2BrF_5 + 30SbF_5 \longrightarrow 10Br_2^+Sb_3F_{16}^- \qquad (2)$$

Glemser and Smalc[16] isolated $Br_3^+AsF_6^-$ by reacting Br_2 with dioxygenyl hexafluoroarsenate according to the equation:

$$2O_2^+AsF_6^- + 3Br_2 \longrightarrow 2Br_3^+AsF_6^- + 2O_2 \qquad (3)$$

They also reacted bromine pentafluoride, bromine and arsenic pentafluoride giving:

$$BrF_5 + 7Br_2 + 5AsF_5 \longrightarrow 5Br_3^+AsF_6^- \qquad (4)$$

The Br_3^+ cation was identified by a strong absorption at 300 n m with a shoulder at 375 n m in its electronic spectrum. The preparation of $Br_3^+SbF_6^-$ was performed in this work using a similar method to that employed by Glemser and Smalc, in this instance $O_2^+SbF_6^-$ was used as the oxidant.

Chlorine Cations.

There is no evidence for chlorine cations even in the strongest superacid.[17] There is evidence for Cl_3^+ in the solid $Cl_3^+AsF_6^-$; this is formed according to the equation:

$Cl_2+ClF+AsF_5 \xrightarrow{203K} Cl_3^+AsF_6^-(s)$. The Cl_3^+ cation was identified[18] by Raman spectroscopy at 197K. At room temperature the solid $Cl_3^+AsF_6^-$ undergoes complete decomposition to give Cl_2, ClF and AsF_5

Group VI : Tellurium Cations.

Bjerrum and Smith studied the reaction of tellurium tetrachloride with tellurium in molten $AlCl_3$-NaCl.[19,20] This reaction gave a purple melt, which the authors claimed to contain the species Te_4^{2+} formed according to the equation:

$$7Te + Te^{4+} \longrightarrow 2Te_4^{2+} \qquad (5)$$

X-ray crystallographic studies of $Te_4^{2+}(AlCl_4^-)_2$ and $Te_4^{2+}(Al_2Cl_7^-)_2$ obtained from the melts mentioned in equation 5 confirmed the presence of Te_4^{2+}.[21] The crystal structures of these two compounds showed that the Te_4^{2+} ion lies on a centre of symmetry and is almost exactly square planar. The Te-Te distance is 2.66 Å which is significantly

shorter than the Te-Te distance of 2.864 Å which is found in the spiral chain in elemental tellurium.[22] This is consistent with a structure exactly analogous to that for Se_4^{2+} in which each bond has approximately 25% double bond character. A representation of the Te_4^{2+} cation is shown in Figure 1.1

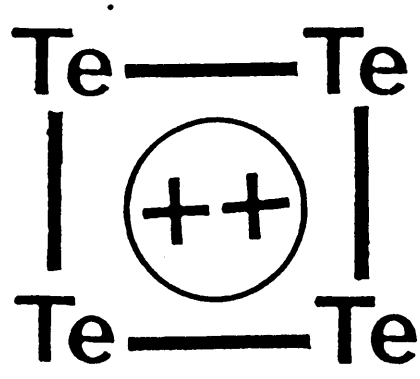
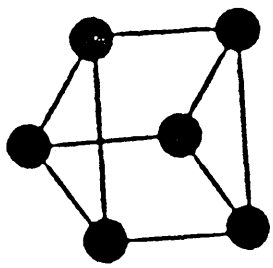


Figure 1.1 The Te_4^{2+} Cation.

Solutions of Te in various acids have also been investigated.[23,24] When Te was dissolved in sulphuric acid, fluorosulphuric acid, or oleum, red solutions were produced, which evolved SO_2, this indicated that the Te was oxidised. It appears that SO_3 did the oxidising in these solutions. The red solutions had electronic spectra identical to those of the melts mentioned earlier containing $Te+TeCl_4$. Conductimetric and cryoscopic measurements of the solutions led to the conclusion that the species responsible for the red colour was Te_4^{2+}. If the red acidic solutions of Te_4^{2+} are heated, or if the oleum is strong enough i.e. ca. 45% SO_3 added to 100% H_2SO_4 a colour change from red to yellow occurs.[20] Increase in the SO_3 concentration both increases the acidity of the medium and provides stronger oxidising conditions, both of which result in the formation of Te_6^{4+}.

The colour change from red to yellow occurs when $S_2O_6F_2$ and $S_2O_8^{2-}$ are used to oxidise Te_4^{2+} in the acidic solvents H_2SO_4 and HSO_3F. Earlier work on the yellow species formulated it as Te_n^{n+} where n was even, and tellurium was in the +1 oxidation state. These studies established that the species could not be Te_2^{2+}, but was probably Te_4^{4+} although Te_6^{6+} and Te_8^{8+} could not be discounted.[24,25] It has now been shown by X-ray crystallography that the Te_n^{n+} species is the cluster cation Te_6^{4+}.[26,27] It has a trigonal prismatic arrangement of the tellurium atoms (Figure 1.2).

Figure 1.2



Structure of the Te_6^{4+} cation.

1.2 Cation Formation in Basic Media.

By using a non-aqueous Lewis base solvent many solvated metallic cationic species can be formed. A useful route to the generation of solvated cations from metals and non metals is by using covalent high oxidation state fluorides as oxidising agents and acetonitrile (MeCN) as solvent.[28] The hexafluorides of molybdenum, tungsten and uranium are useful reagents to use in acetonitrile. The hexafluorides, MoF_6, WF_6 and UF_6 have octahedral arrangements of six fluorine atoms around the central metal.[29] The oxidising abilities of MoF_6, WF_6 and UF_6 have been studied by several methods, for example, ion cyclotron resonance spectroscopy,[30] molecular beam reactions with alkali metals,[31] thermochemistry of hexafluorometallate(V) salts[32] and effusion mass-spectrometry.[33] The values obtained for the electron affinities using these techniques differ slightly from each other depending on the technique used, but the general trend of electron affinities is:

$$UF_6 > MoF_6 > WF_6$$

In acetonitrile the hexafluorides behave as one electron oxidising agents. These oxidising agents are easily handled under vacuum and readily dissolve in acetonitrile. The anions UF_6^-, MoF_6^- and WF_6^- formed from redox reactions have characteristic spectra and are easily detected using spectroscopic techniques such as, electronic, Raman and infra red spectroscopies. The ν_1 ; ν_2 and ν_5 vibrations of the octahedral hexafluoroanions are observed by Raman and the ν_4 and ν_3 vibrations by infra red spectroscopy. The presence of the UF_6^- anion can be confirmed by its near infra red, visible electronic spectrum; it has several

sharp bands in the region 1600 - 500 nm which are very characteristic.

A study of redox reactions and cyclic-voltammetry involving the three hexafluorides and other oxidising agents in MeCN[28] gave the following order of oxidising ability:

$$UF_6 > MoF_6 > NO^+ > Cu^{2+} > WF_6.$$

The hexafluorides UF_6, MoF_6 and WF_6 in MeCN oxidise a large number of transition and post transition metals to give salts containing solvated metal cations with discrete fluoroanions, where the metal is solvated by MeCN molecules, and the hexafluoride forms the MF_6^- counter anion. The oxidation states of the metal cations formed depend on the hexafluoride used. Thallium metal is oxidised by UF_6 or MoF_6 to Tl(III), but, to Tl(I) by WF_6.[34,35] Silver metal is oxidised by MoF_6, WF_6, UF_6 or the nitrosonium cation in acetonitrile to give the solvated silver(I) cation $Ag(NCMe)_2^+$. When acetonitrile ligands of the cation $Ag(NCMe)_2^+$ are replaced by pyridine, the cations formed can undergo further oxidation by UF_6 or MoF_6 to give Ag(III) compounds. The Ag(III) cations are strong oxidising agents in MeCN and will oxidise the solvated copper(I) cation and molecular iodine to give copper(II) and $I(NCMe)_2^+$ respectively.[36]

The iodine (+1) cation solvated by acetonitrile has often been postulated to exist, most recently as one component of an electrical energy storage cycle.[37] The first examples of isolated salts containing the iodine(I) cation were prepared from the oxidation of

molecular iodine in MeCN by MoF_6 or UF_6 to give $[I(NCMe)_2][MF_6]$ (M = Mo, U) as isolable compounds.[38] From their reactions[39] it was apparent that the chemistry of $[I(NCMe)_2]^+$ was very different from that of the well known $[I(py)_2]^+$ cation. This aspect of their chemistry will be dealt with in more detail in Chapter 2.

1.3 Acetonitrile - A Convenient Solvent for Cation Formation.

Inorganic synthesis in aqueous media often presents problems because of the acidities and basicities available in water. Many compounds can be formed outwith the redox range available when water is used as solvent. By using extremely acidic or basic media unusual cationic or anionic species can be formed, the stabilities of which depend on the availability, or the non-availability of basic or acidic species in the solvent. However, handling of these reagents is not so routine and presents a number of difficulties. Superacids present problems due to their highly corrosive nature, an acidic solvent like SO_2 requires low temperatures to work with it safely. Bases such as liquid ammonia require low temperatures to work with it in conventional apparatus. By choosing an organic solvent some of these difficulties can be overcome. A number of protonic and aprotic solvents could be used for formation of cations in non-aqueous media. Liquid ammonia for example is protonic, and self ionises[40] resulting in a solvated proton and a deprotonated anion.

Aprotic solvents which do not involve proton transfer can be divided into three groups.[40] Solvents such as benzene and cyclohexane form the first group. They are non-polar, do not undergo self ionisation and thus generally behave as non-solvating agents.

The second group consists of polar solvents that do not ionise to an appreciable extent. Examples are MeCN, dimethylsulphoxide (DMSO) and SO_2. They are good coordinating solvents because of their polarity which ranges from low in the case of SO_2 to extremely high (DMSO). The third group consists of solvents which are highly polar and auto ionising such as bromine trifluoride.

When choosing a solvent for inorganic synthesis there is obviously a large choice. Each solvent has its own merits, but ease of handling, non-corrosive properties, convenient liquid range, useful volatility range, useful for spectroscopic work and easily purified are criteria which make a solvent attractive for synthesis. Acetonitrile meets most of these requirements, so it was chosen as the main solvent for this work.

Acetonitrile is a dipolar, aprotic solvent, and has a proven record in exploring the non-aqueous chemistry of cations.[41] The nature of the reagents used in this work, require vacuum line techniques and MeCN is a useful solvent for this approach; its volatility m.p. = 45.7°; b.p. = 81.6° C, make it ideal for handling in greaseless Pyrex systems at ambient temperatures. Its dielectric constant is relatively high, 37.5 at 25°C.[42], and it is therefore a suitable solvent for many ionic compounds. It is easily purified and has a large electrochemical working range of 5.7V. It is a strong enough Lewis base to solvate many high oxidation state covalent fluorides and metal cations, but it can be replaced easily by other bases such as pyridine or ammonia.[43] It has a characteristic yet simple vibrational spectrum and is extremely useful as a solvent in the visible and U.V. regions because it is transparent down to 175nm. The deuterated solvent CD_3CN is readily available and

this enables deuterium exchange or n.m.r experiments to be carried out. All the above properties make MeCN an ideal solvent for the work in this project. Acetonitrile is a donor solvent and the nature of its coordination to metal centres has been reviewed.[44] It coordinates through the lone pair of electrons on the nitrogen, this causes an increase in the stretching frequencies of the C≡N and C-CN bonds compared with those of the free solvent.[45] Useful evidence for the presence of coordinated acetonitrile in the complexes formed is thus provided.

1.4 Electrophilic Halogenation of Aromatic Compounds.

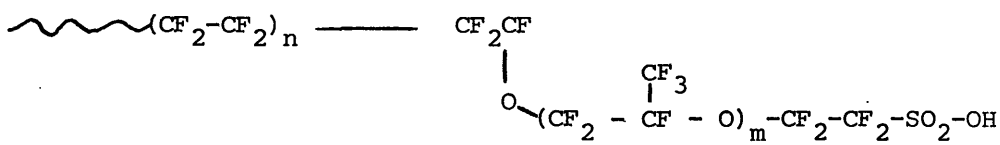
The use of inorganic compounds as reagents in organic synthesis is widespread and in many cases very sophisticated. Electrophilic bromination of aromatic hydrocarbons is a well established procedure which has been known since the beginnings of modern organic chemistry and is discussed in every elementary text book.[46] However, it often involves the aromatic molecules being subjected to severe conditions such as refluxing in oleum at high temperatures or it involves the use of Friedel-Crafts catalysts. These methods have limitations due to energy costs, and large amounts of water-sensitive catalysts are needed which create disposal problems on an industrial scale. The presence of sensitive groups cannot usually be tolerated in these harsh conditions. Covalent compounds of iodine and tellurium, in which the element is in a high oxidation state play an important role in modern organic syntheses, due mainly to the oxidising abilities of the hypervalent halogens.[47,48]

The application of polymers containing functional groups is one of the most important recent developments in organic chemistry.

Using insoluble resins as support for reagents or catalysts has specific advantages. These have been reviewed by Leznoff[49], and a few examples are given below:

1. Ease of by-product separation from main reaction product by simple filtration.
2. Prevention of intermolecular reaction of reactive species or functional groups by simulating high dilution conditions.
3. Removal of a minor component from a large excess of substrate by the insoluble polymer.
4. The possibility of reusing recovered reagents as well as eliminating the use of volatile or noxious substances.

The resin of interest in this work is Nafion. This is a perfluorinated resinsulphonic acid with the general structure in the acid form



Nafion H

Nafion H is used as an acid catalyst for many organic synthesis systems; a recent review[50] cites over 100 references for its use. Replacement of the hydrogen of the sulphonate group by a bromine or chlorine atom results in the formation of the hypochlorite or hypobromite groups[51] according to the equations:

$$\text{Nafion-H} + \text{ClF} \xrightarrow[\text{18h ClF}]{\text{162 to 243 K}} \text{Nafion-Cl} + \text{HF} \qquad (6)$$

$$\text{Nafion-Cl} + \text{BrCl} \xrightarrow[\text{BrCl}]{\text{223 to 273K}} \text{Nafion-Br} + \text{Cl}_2 \qquad (7)$$

It was previously shown that the perfluoroalkanesulphonic acids CF_3SO_2OH and $n\text{-}C_4H_9SO_2OH$ can be converted to the corresponding hypohalites $R_F SO_2OX$ (X = Cl, Br) in excellent yield.[52] These hypohalites proved to be remarkable sources of electrophilic halogen and were studied extensively by Desmarteau et al.[53,54] It is possible that these Nafion hypohalites will react similarly to the perfluoroalkanesulphonic acids and Nafion-X (X = Cl, Br) offers the prospect of the functionalisation of the resin. These resin hypohalites should prove useful in many ways from synthesis to fundamental studies of ionomers.

Recently bromine monofluoride (BrF) has been used as a brominating agent[55]; it does not require high temperatures or catalysts, but has the disadvantages of requiring a fluorine source, and is only stable at low temperatures. The BrF was prepared in situ by passing dilute fluorine (10% F_2 in N_2) through a cold ($198K$) suspension of bromine in $CFCl_3$. A solution of an activated aromatic substrate, such as toluene, anisole etc in $CHCl_3$ at $198K$ was added to excess BrF solution. Anisole was brominated quantitatively (para:ortho 4:1). Toluene was monobrominated in >90% yield (para:ortho 1:1).

From the preceding paragraphs it is clear that incorporation of a bromine atom into a reagent or resin in which it becomes electropositive may have potential as a reagent for organic chemists. The work involved in this project, where cationic species with simple ligands and discrete anions where the goals, could possibly provide such a reagent. It should be capable of reacting with an organic

substrate under mild conditions, be easily handled, and should be compatible with a wide range of organic solvents. It needs to be reactive yet have sufficient kinetic stability to be useful in organic synthesis. Work reported while the present work was in progress showed that $[(quinuclidine)_2Br][BF_4]$ can be used as a reagent in the presence of silver(I)tetrafluoroborate ($AgBF_4$) to oxidise alcohols to carbonyl compounds, particularly secondary alcohols to ketones.[56] The iodine analogue $[(quin)_2I][BF_4]$ has recently been made[57] and this will probably be used in a similar manner as a potential reagent.

CHAPTER TWO

STRUCTURAL CHARACTERISATION OF

$[I(NCMe)_2][MoF_6]$ in MeCN.

Introduction

The compound $[I(NCMe)_2][MoF_6]$ in MeCN solution was shown to react very differently from the well known $[I(py)_2]^+$ cation. For example, the $[I(NCMe)_2][MoF_6]$ salt in MeCN proved to be a strong enough oxidising agent to oxidise NO to NO^+ and solvated Cu^+ to solvated Cu^{2+}. It also iodinated benzene and its derivatives at room temperature giving mixtures of products. The nature of the products suggested strongly that the reactions were occurring via an electrophilic substitution mechanism presumed to involve solvated I^+.[39] By using iodine and molybdenum EXAFS the structure of $[I(NCMe)_2][MoF_6]$ in MeCN solution could be elucidated and this would enable the chemistry of the cation to be fully understood. The EXAFS data would provide a coordination number for the cation and prove if MeCN ligands were in fact the only species in the primary coordination sphere.

The compounds $[I(py)_2][NO_3]$, $[I(py)_2][MoF_6]$ and $[Ag(py)_4][MoF_6]$ have also been studied by EXAFS in order to obtain comparative data. An X-ray crystallographic study of $[I(py)_2][I_3].2I_2$ indicates that the $[I(py)_2]^+$ cation is linear and centrosymmetric.[58] ^{129}I and ^{127}I Mössbauer spectroscopy of $[I(py)_2][NO_3]$ have been interpreted on a similar basis, the I-N bonding being largely of p-character.[59] Although the structure of $[Ag(py)_4][MoF_6]$ has not been determined, the $[Ag(py)_4]^+$ cation in the perchlorate salt is tetrahedral[60] and the spectra and properties of the hexafluoromolybdate(V) salt in the solid state and in MeCN solution are consistent with the presence of discrete ions.[61]

RESULTS

Iodine K-edge EXAFS

Analyses of the iodine EXAFS are constrained by the small number of light back-scatterers and the large core-hole relaxation. However the first shell, iodine-nitrogen distances, could be derived from the Fourier-filtered data. They are given in Table 2.1. Reasonably good final fits of the EXAFS were obtained by assuming that the distances in Table 2.1 were little affected by inferior background subtractions and truncation errors, and that the ligand units are fairly rigid. The analyses indicate that multiple scattering plays an important part in the outer shell back-scattering. They are consistent with iodine being two coordinate in all cases.

Table 2.1 Iodine-Nitrogen Distances (Å)

Compound	Solid	MeCN solution
$[I(py)_2][NO_3]$	2.21 (0.011)	2.16 (0.020)
$[I(py)_2][MoF_6]$	2.21 (0.017)	2.21 (0.013)
$[I(NCMe)_2][MoF_6]$	2.17 (0.015)	2.14 (0.017)

The I-N distances determined for the $[I(py)_2]^+$ cation are reasonable in comparison with the value of 2.16 Å found in the X-ray study of $[I(py)_2][I_3].2I_2$.[58] This latter distance could not be determined very precisely, and may be in error by as much as ±0.1 Å. Due to the experimental limitations of the X-ray analysis and the constraints on the EXAFS analyses, speculation as to the effect of different anions and the change of physical state on I-N is not

justified. I-N distances in the $[I(py)_2]^+$ and $[I(NCMe)_2]^+$ cations are virtually identical at 2.18 (3) Å. Attempts to observe iodine EXAFS at the L3-edge using fluorescence detection were unsuccessful due to instrumental difficulties.

Molybdenum K-edge EXAFS.

EXAFS spectra at the molybdenum K-edge, obtained from the same samples as those used for the iodine measurements, showed only one shell, apart from the solid $[I(py)_2][MoF_6]$ sample which showed a beating. The one shell was due to the fluorine atoms surrounding the molybdenum and the beating was due to another back-scattering atom at a slightly different distance. Analysis of this spectrum showed a shell at approximately 1.6 Å. This is assigned to a Mo=O group, arising from partial hydrolysis of the sample, by comparison with Mo-O (terminal) distances of 1.62(1) and 1.65(1) Å in solid $(MoF_4O)_\infty$ [62] and of 1.650(7) Å in gaseous MoF_4O.[63] The absence of this feature in the other samples was taken as an indication that significant hydrolysis had not occurred. The molybdenum-fluorine distances determined are given in Table 2.2.

Salts of the MoF_6^- anion do not appear to have been studied by X-ray crystallography; an X-ray powder study of $NaMoF_6$ gave Mo-F 1.74 ± 0.03 Å.[64] This data is almost 30 years old and was not determined with the same precision available now to crystallographers, due to better experimental facilities; powder data also have limitations compared to single crystal determinations. The most obvious comparisons to make are with molybdenum penta- and hexafluorides. The Mo-F (terminal) distances in solid $(MoF_5)_4$[65] are 1.78 (average)

Table 2.2

Molybdenum - Fluorine Distances Å	
$[I(py)_2][MoF_6]$ in MeCN	1.77 (0.013)
$[I(NCMe)_2][MoF_6]$ in MeCN	1.77 (0.009)
$[Ag(py)_4][MoF_6]$ solid	1.79 (0.011)

and in a gas phase study by electron diffraction[66] $(MoF_5)_3$ Mo-F 1.814(6) Å. Mo-F distances in solid, orthorhombic MoF_6 at 193 K are in the range 1.766(12) - 1.861(29), average 1.812(8) Å and at 77 K the average distance is 1.824(7) Å.[67] In the cubic, plastic phase at 266 K Mo-F is 1.802(14)[68] and in the gas phase it is 1.820(3).[69]

The EXAFS is consistent with the MoF_6^- being present as an uncoordinated anion. There is no evidence for a Jahn-Teller distortion arising from the t_{2g}^1 ground state, but this is not surprising since any distortion would be expected to be very small, thus undetectable by EXAFS. Previous workers in this department have been unable to detect e.p.r. signals from MoF_6^- salts in frozen MeCN solutions at 77 K, which is consistent with a lack of distortion.

DISCUSSION

This EXAFS study has provided good evidence for the presence of discrete ions in the compounds $[I(NCMe)_2][MoF_6]$ and $[I(py)_2][MoF_6]$ in MeCN solution. Similar behaviour for metal cation, fluoroanion salts in MeCN has been found. For example the ^{31}P n.m.r. spectrum in CD_3CN of the complex $[Cu(NCMe)_5][PF_6]_2$, having the paramagnetic cation, Cu^{2+}, and the diamagnetic anion, PF_6^-, consists of a 1:6:15:20:15:6:1 septet due to the coupling with six equivalent fluorine nuclei and is chacteristic of the free PF_6^- anion.[61] Another example where similar behaviour is found is the complex $[Ag(py)_4NCMe][MoF_6]_3$, in which the Ag^{III} cation is diamagnetic and the MoF_6^- anion is paramagnetic. The paramagnetic anion MoF_6^- does not seem to have any noticeable effect on the n.m.r resonances of the complex cation.[36] However a recent ^{205}Tl n.m.r. study[71] has shown some degree of ion pairing involving thallium(I) fluoro-metallates, were PF_6^-, WF_7^-, MoF_6^- and UF_6^- are the anions in acetonitrile solution. The paramagnetic anion UF_6^- has a pronounced effect on the ^{205}Tl resonance in the Tl^+ salt, but its effect on Tl^{3+} is very small. It is suggested that Tl^{3+} is effectively stabilised by MeCN and that direct ion pairing is unimportant. Maybe ^{205}Tl n.m.r provides a more sensitive probe for slight anion-cation interactions, than other techniques, an X-ray crystal study would be less ambiguous. However no single crystals could be obtained from the iodine compounds.

The vibrational spectra of the $[I(NCMe)_2][MoF_6]$ complex is consistent with the presence of octahedral MoF_6^- and coordinated C≡N. A linear N-I-N arrangement for the cation in the solid state has been

suggested previously.[38,39] This was based on the low frequency bands at 174 (Raman) and 220 cm^{-1} (IR) assigned to symmetric and asymmetric N-I-N stretching modes respectively. This is supported by the iodine EXAFS, both in the solid and in solution.

The three IR bands in the C≡N stretching region, are more than can be accounted for on the basis of a single type of coordinated MeCN, but it is considered that the extra bands reflect site-symmetry effects in the solids and do not indicate $I(NCMe)_2^+$ is non centrosymmetric.[38] Linear structures for $[I(L)_2]^+$ L = MeCN or py, are unexceptional in the sense that they could be predicted by the V.S.E.P.R. approach to stereochemistry. The I-N bond distances in the two cations are similar and analogous to the situation when these ligands are bound to Cu^I, cis $Pt^{II}Cl_2$ and BF_3 Lewis acids. Bond distances for these complexes determined by X-ray crystallography are given in Table 2.3.

The $I(NCMe)_2^+$ cation is shown to be a very good oxidising agent, for example it oxidises the solvated Cu^I cation; NO and thallium metal to give the solvated Cu^{II} cation, NO^+, and a mixture of solvated cations of Tl^I and Tl^{III} respectively. Whereas $[I(py)_2]^+$ does not perform these oxidations. Pyridine is a stronger ligand displacing coordinated MeCN from a mixture of $[I(NCMe)_2][MoF_6]$ and pyridine in MeCN solutions, and is more effective in stabilising iodine(+1) than is MeCN. This phenomenon is observed for metal cations, for example Cu^{II} and Ag^{III} are stabilised with respect to their monopositive oxidation states by ligated pyridine more effectively than by ligated MeCN.[61,28] Pyridine has stabilised I^+ with respect to reduction more effectively than MeCN. A cyclic

Table 2.3

Structural data for some MeCN and py Complexes.

Compound	M-L distance (Å)	Ref.
$[Cu(NCMe)_4][ClO_4]$	1.95(1) - 2.02(1)	73
$[Cu(py)_4][ClO_4]$	2.046(4)	74
$cis[Pt(NCMe)_2Cl_2]$	1.977(12) - 1.981(11) 1.95(2), 1.99(2)	75
$cis[Pt(py)_2Cl_2]$	2.04(1) 2.01(1)	76
BF_3NCMe	1.630(4)	77
$BF_3(py)$	1.602(4)	78

voltammetry study has shown that I^+ is stabilised with respect to reduction by strong ligands which have displaced coordinated MeCN from $I(NCMe)_2^+$. The half wave potentials, $E_{\frac{1}{2}}$ (V) relative to Ag^+/Ag^o show I^+/I as, $I(NCMe)_2^+$ +1.1V, $I(Me_2S)^+$ + 0.32, $I(tmtu)_2^+$ + 0.28, $I(bipy)^+$ + 0.25, $I[(14)\text{-}aneN_4]$ + 0.12, $I[(15)\text{-}aneN_4]$ + 0.12 V.[70] This poor stabilisation of iodine(+1) by MeCN along with the small steric requirement of two MeCN ligands in the transition state of an electrophilic iodination is thought to be the cause of its iodinating ability towards benzene derivatives. The results from this study clearly show there are analogies between iodine(+1) and metal cation coordination chemistry. This work provided a basis for further research into iodine(+1) chemistry. By characterising the structure of the I^+ cation in solution, it was realised that ligand substitution could take place giving a number of I^+ cations with stabilising ligands. It had previously been shown that iron(II) coordination chemistry could be conveniently studied in acetonitrile using various simple, N, P and S- donor ligands,[70,43] and the iodine work could be studied on a similar theme.

CONCLUSION

EXAFS has provided structural evidence for the existence of the $I(NCMe)_2^+$ cation. The chemistry of iodine(+1) in MeCN can be placed on a firm basis. The combination of the EXAFS study and the subsequent substitution reactions[70], shows there are analogies between iodine(+1) and metal cation coordination chemistry. EXAFS has been shown to be a useful technique in this area of work where it is not always possible to obtain single crystals. The cells designed enabled very hygroscopic compounds to be studied, these may have further uses. By stabilising iodine(+1) by macrocyclic ligands a higher oxidation state may be obtained.

EXPERIMENTAL

The compounds $[I(NCMe)_2][MoF_6]$, $[I(py)_2][MoF_6]$[39] $[I(py)_2][NO_3]$[72] and $[Ag(py)_4][MoF_6]$[61] were prepared using the published procedures. All operations, apart from those involving $[I(py)_2][NO_3]$, were carried out *in vacuo* or in the glove box. The solids were ground using an Agate mortar and pestle, boron nitride (Fluka) was added to dilute the solids by approximately 50% by volume. The mixture was pressed between pieces of Mylar film (thickness 0.07mm), the sample thickness being determined by the aluminium spacer (thickness 1mm), Mylar-aluminium seals were made with quick setting Araldite adhesive. Solutions were made by distilling the appropriate amount of acetonitrile onto the solids contained in single limbed vessels. The solutions were then loaded into the EXAFS solution cells (Figure 2.1) in the glove box. Solution concentrations were as follows, $[I(NCMe)_2][MoF_6]$ ca 0.18 mol dm^{-3}, $[I(py)_2][MoF_6]$ ca 0.2 mol dm^{-3}. The cells were stored at 195 K until spectra were recorded.

Iodine and Molybdenum EXAFS spectra were obtained in the transmission mode at the K-edge for both elements by Dr. A. Steel, Daresbury Laboratory under the auspices of the SERC SRS EXAFS service. Solids were examined over a range of temperatures usually from 223 K to room temperature, and solutions were examined at room temperature. Data analysis, by Dr. A. Steel employed phase shifts calculated by *ab initio* methods using the MUFPOT program (Daresbury software). To obtain satisfactory fits of the iodine EXAFS it was necessary to include calculated multiple scattering contributions.

EXAFS Cells.

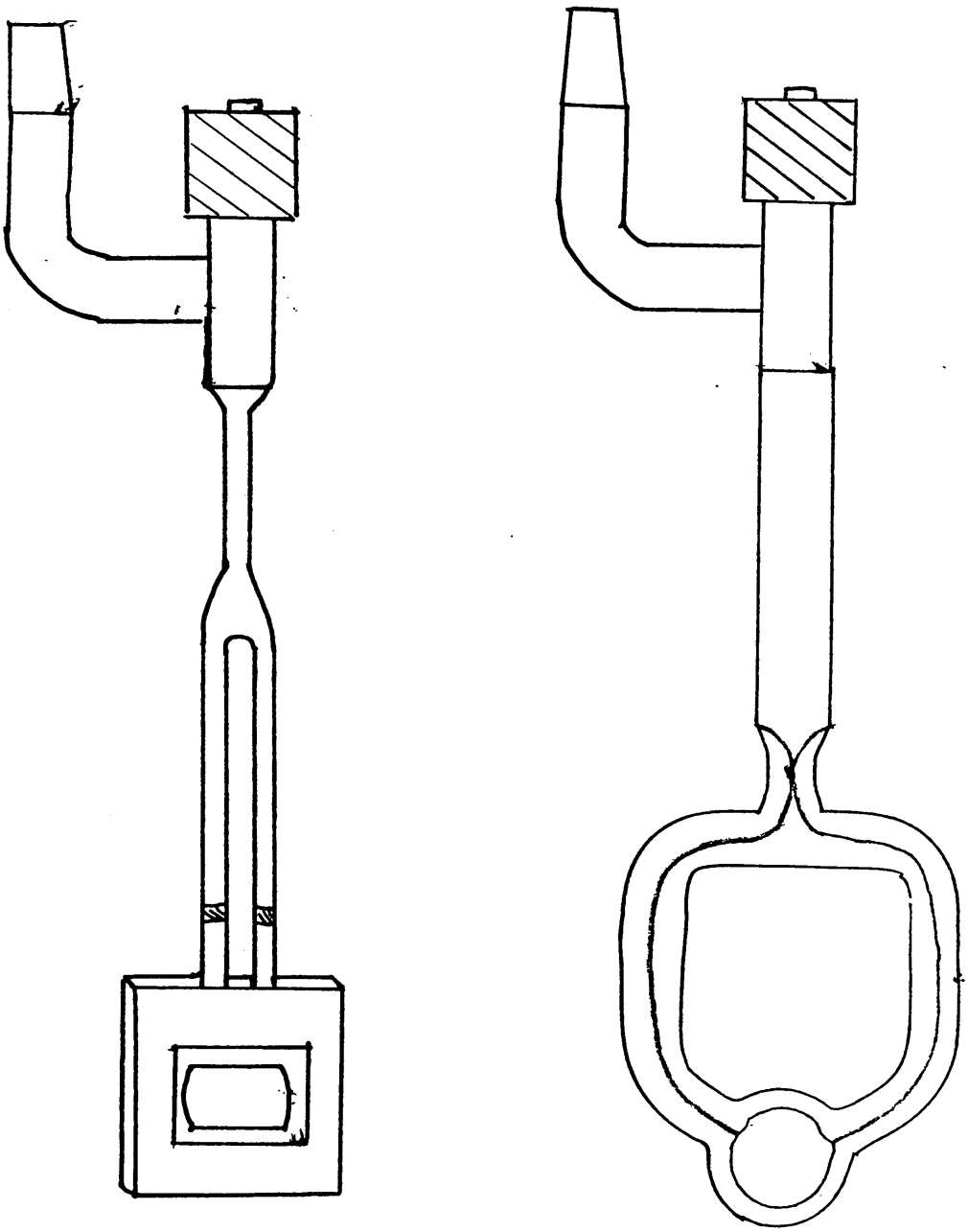


Figure 2.1

CHAPTER THREE

OXIDATION OF BROMINE BY URANIUM HEXAFLUORIDE IN ACETONITRILE.

Introduction

A study of the cationic species possibly generated in the anodic cleavage of C-Br bonds during the course of anodic oxidation of alkyl bromides in MeCN on platinum led to postulation that an ionic bromine species was being formed.[79] The U.V. spectrum of a solution of Br_2 in MeCN electrolysed at 1.6V (versus Ag/Ag^+) had a band λ_{max} 268 nm which is not derived from the solvent (210nm) or from Br_2 (418nm). This indicated the possibility of the formation of a new species between Br_2 and MeCN. The following structures have been proposed for the species formed

$$[(MeCN)_2Br]^+ [Br_3]^- \qquad (1)$$

$$[MeCNBr]^+ [Br_3]^- \qquad (2)$$

The explanation for the formation of these species (1) and (2) was derived from an earlier suggestion by Mulliken[80], where he suggested a mechanism for the formation of charge transfer complexes between acetonitrile and halogens as in Scheme 3.1.

$$CH_3CN + X_2 \longrightarrow CH_3CN.X_2 \qquad \text{(fast)}$$

$$CH_3CN.X_2 \longrightarrow CH_3CNX^+X^- \qquad \text{(slow)}$$

$$CH_3CNX^+X^- \longrightarrow [CH_3CNX]^+X^- \qquad \text{(fast)}$$

$$X_2 + X^- \longrightarrow X_3^- \qquad \text{(fast)}$$

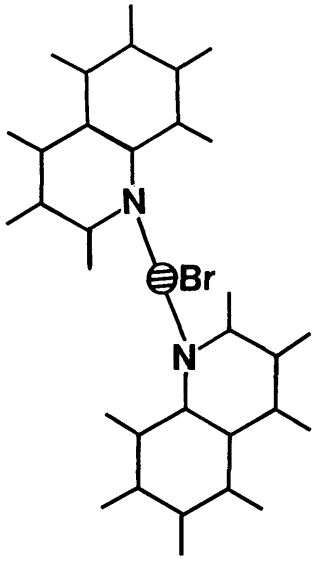
Scheme 3.1

The authors believe two MeCN molecules could be coordinated to the positive bromine and the last two reactions in Scheme 3.1 could be replaced by each of equations (3) and (4).

$$2CH_3CNX^+X^- \longrightarrow [(CH_3CN)_2X]^+ + X_3^- \quad (3)$$

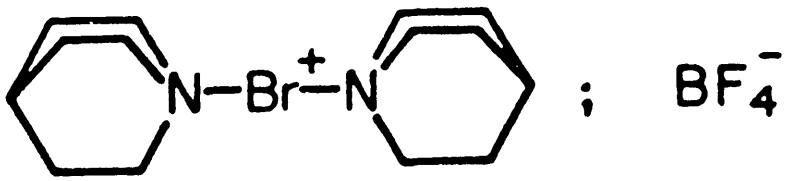
$$CH_3CNX^+X^- + X_2 \longrightarrow [CH_3CNX]^+ + X_3^- \quad (4)$$

Cations of the type $[BrL_2]^+$ (L = quinoline[81], or quinuclidine[82]) have also been prepared, their structures being determined by X-ray crystallography. $[Br(quinoline)_2][ClO_4]$ is formed by reacting bromine with a solution of silver perchlorate and quinoline in chloroform. The principal features in the determination are the cations, there are two independent ions which have a Br^+ ion coordinated linearly by two quinoline molecules with Br-N 2.10-2.18 Å. The coplanar quinoline molecules are related by approximate centres of symmetry at Br. This was the first reported structure of a bromine containing cation to be examined.



Structure of Bis(quinoline)bromine perchlorate.

By reacting quinuclidine and Br_2 in dichloromethane, $[Br(quinuclidine)_2][Br_3]$ is obtained. Adding $AgBF_4$ in MeCN gives the $[BF_4]^-$ salt. $[Br(quinuclidine)_2][BF_4]$ has a linear cation symmetric about the Br, bond lengths being Br-N, 2.156 and 2.120 Å.



Structure of Bis(quinuclidine)bromine tetrafluoroborate.

By oxidising bromine in MeCN using chemical methods, bromine cations, possibly $[Br(NCMe)_2]^+$ could be formed analogous to the $[I(NCMe)_2]^+$ cation discussed in Chapter 2. Relatively strong oxidising agents in MeCN would need to be used, UF_6 and MoF_6 fulfilled this criterion. ($E^{1}/_{2}$ for UF_6, UF_6^- ca 2.3V, MoF_6, MoF_6^- ca 1.6V in MeCN versus Ag, Ag^+ [28]). Oxidation of bromine did occur with UF_6 in MeCN, but the product did not contain $[Br(NCMe)_2]^+$. No reaction occurred between MoF_6 and Br_2 in MeCN, this is the first example of different behaviour occurring between these two strong oxidising agents in MeCN.[83]

Reaction of Molecular Bromine with Uranium Hexafluoride.

Uranium hexafluoride was added to a frozen solution of molecular bromine in acetonitrile, mole ratio Br_2: UF_6 > 3:1. As the solution warmed to room temperature a decrease in the intensity of the red colour was observed. Obtaining a product from the reaction proved difficult at first, until the correct conditions were achieved. Several preparations were attempted using different amounts of reagents and varying temperatures. The reaction is exothermic, this caused extensive polymerisation of the solvent giving an insoluble jelly like polymer. When UF_6 was in excess that is more UF_6 than required for a UF_6:Br_2 mole ratio 2:1 the solvent was polymerised. By keeping the mixture below 243 K this problem was overcome, but the unreacted UF_6 attacked the product, when the solvent was removed during isolation, acetonitrile being more volatile than UF_6, was removed first. To overcome these problems it was found that an excess of bromine that is $\frac{1}{2}Br_2$:UF_6 > 3:1 mole ratio acted as a heat sink and stopped the solvent from polymerising. The solid obtained using this method was soluble in acetonitrile giving a pale green solution. The solid could be stored for very long periods in vacuo at 273 K, but slow decomposition giving Br_2 as one product occurred; this was identified by redissolving the product in MeCN and observing the Br_2 band at 418 nm in its electronic spectrum. Decomposition was more rapid (observable after 12 hours) in MeCN solution at room temperature, bromine being identified by its electronic spectrum.

Identification of the Product from Br_2 and UF_6 in MeCN.

The pale green solid obtained from the reaction of Br_2 and UF_6 in MeCN dissolved easily in MeCN. The solid isolated had the empirical formula $C_6H_9BrF_6N_3U$. By comparing the electronic spectrum of the solid in MeCN solution with literature values, the presence of the hexafluorouranate(V) anion was indicated. The bands found were very similar to those for solid caesium hexafluorouranate(V)[84], tetraphenylarsonium hexafluorouranate(V), $[AsPh_4][UF_6]$ (in solid and in MeCN solution)[85] and thallium(III) hexafluorouranate(V) in MeCN solution.[36] The point group of the UF_6^- ion is O_h, this would lead to the presence of only four bands for pure electronic transitions. The remaining features of the spectrum are assigned to vibronic coupling. The solids electronic spectrum in MeCN is shown in (Figure 3.1) and the bands and assignments are tabulated in (Table 3.1).

Vibrational spectra indicated the presence of the $[UF_6]^-$ anion, ν_1 and ν_3 of $[UF_6]^-$ at 619 cm^{-1} (Raman) and 515 cm^{-1} (i.r)[35] respectively were found. Raman spectra were recorded in MeCN solution and in the solid state; the solutions fluoresced and Br_2 was released. The Raman spectra of the solids were recorded at ambient temperature and at 10 K, to try to stop sample decomposition. A very noticeable feature of the vibrational spectra was the complete absence of C≡N vibrations, which are very characteristic of compounds containing coordinated MeCN. Strong bands at 1627, 1580 and 1520 cm^{-1} were compared with s-triazine type ring systems. Bands in these positions are very characteristic of a ring system containing C=N groups.[86] The vibrational spectra are tabulated in (Table 3.2). (The vibrational spectra of s-triazine is tabulated in Table 3.4 for comparison).

$[Br(C_6H_9N_3)][UF_6]$ in MeCN

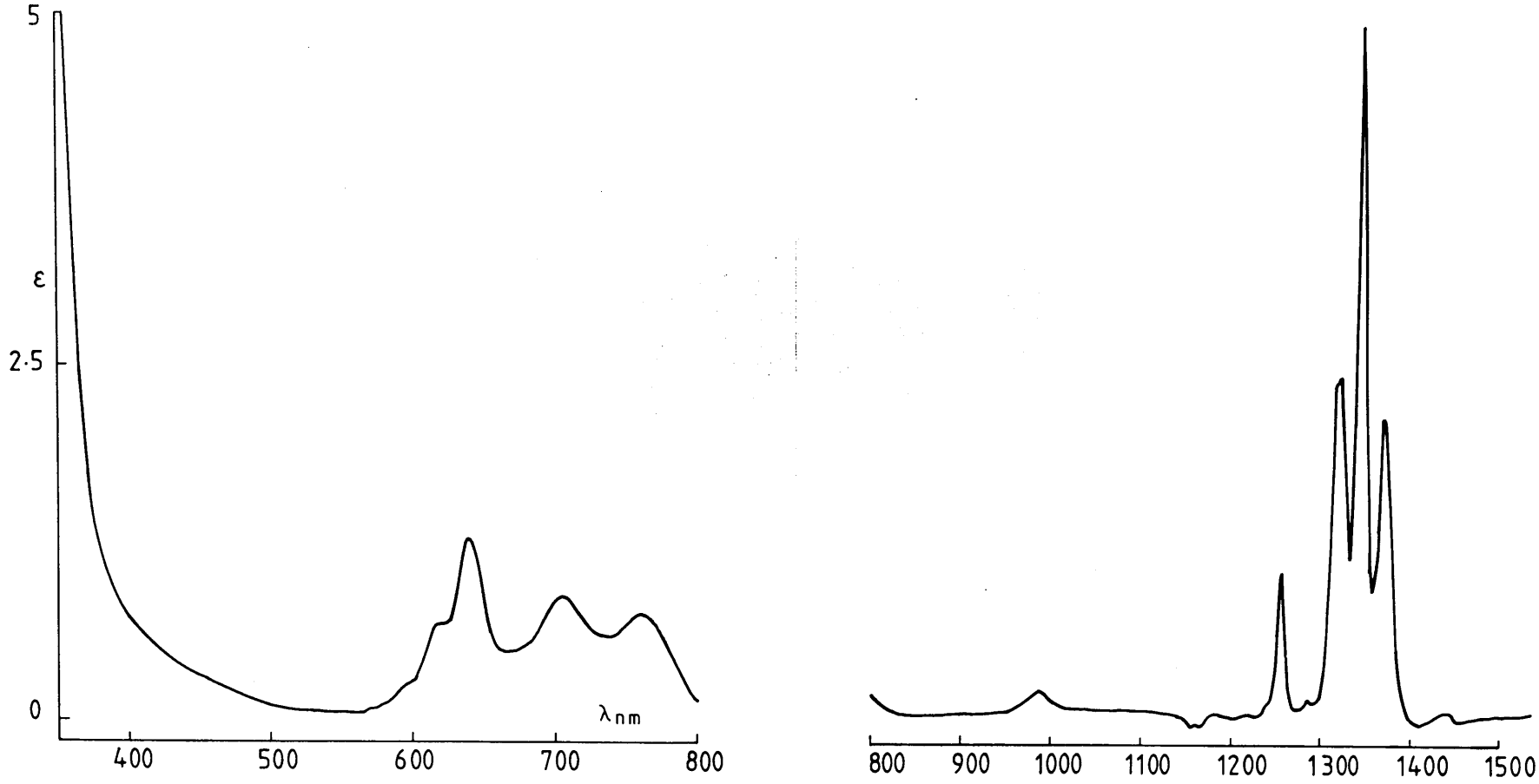


Figure 3.1

Table 3.1 Electronic Spectrum of $[Br(C_6H_9N_3)][UF_6]$ in MeCN.

$[Br(C_6H_9N_3)][UF_6]$			$[Tl(MeCN)_5][UF_6]_3$ [35]		
ν cm^{-1}	vibrational mode	electronic transition	ν cm^{-1}	vibrational mode	electronic transition
7267	ν_4		7290	ν_4	
7412		$\Gamma 7' \leftarrow \Gamma 7$	7425		$\Gamma 7' \leftarrow \Gamma 7$
7535	ν_4		7580	ν_4	
7564					
7739					
7930	ν_3		7950	ν_3	
10,121					
13,157			13,175		
14,184		$\Gamma 8' \leftarrow \Gamma 7$	14,175		$\Gamma 8' \leftarrow \Gamma 7$
15,674			15,650		
16,207		$\Gamma 6 \leftarrow \Gamma 7$	16,150		$\Gamma 6 \leftarrow \Gamma 7$

Table 3.2 Vibrational Spectra of $[Br(C_6H_9N_3)][UF_6]$

Infrared (CM^{-1})	Assignment	Raman $\Delta\nu cm^{-1}$	Assignment
3160 m			
2985 s	CH str		
2940 s	CH str	2954 (2)	CH str
2604 m			
1850 w			
1627 s	C=N str		
1580 s	C=N str		
1520 s	C=N str		
1455 s	CH_3 def	1464 (1)	CH_3 def
1435 m	CH_3 def		
1420 m	CH_3 def	1414 (8)	CH_3 def
1380 m	CH_3 def		
1370 s	CH_3 def		
1305 m		1058 (10)	
1028 s	CH_3 rock	1033 (8)	CH_3 rock
950 m	C-C str	964 (3)	C-C str
740 m			
		679 (1)	
		619 (13)	$\nu_1[UF_6]^-$
605 s		606 (5)	
		525 (6)	
515 vs	$\nu_3[UF_6]^-$		
440 m			
365 m		373 (1)	
290 m			

Str = stretching mode, Relative intensities in brackets.

def = deformation s = strong m = medium

w = weak vs = very strong

Table 3.3

Mass Spectrum of $[Br(C_6H_9N_3)][UF_6]$

m/z	Relative Intensity	Assignment
283	3.1	
281	6.1	
279	2.9	$C_6H_7{}^{79}Br_2N_3$
201	22.4	$C_6H_8{}^{79}BrN_3$
203	21.9	
160	7.1	$C_4H_5{}^{79}BrN_2$
162	6.8	
123	21.5	$C_6H_9N_3$
121	5.1	
119	5.5	$C_2H_2{}^{79}BrN$
82	33.6	$C_4H_6N_2$
67	6.8	C_4H_5N
66	2.8	C_4H_4N
54	9.8	C_3H_4N
42	100	C_2H_4N
41	28.9	C_2H_3N

Table 3.4 Vibrational Spectrum of s-triazine[86]

Infrared (cm^{-1})	Raman $\Delta\nu$ cm^{-1}	Class
	3046	A'
3025 vw	3025	E'
1956 vw		
1850 vw		
1775 vw		
1560 vs	1560 (1)	E'
1410 vs	1404	E'
1170 m		A_2''
	991 (4)	A_1
	921 (½)	E"
735 s		A_2''
673 ms	676 (2)	
	594 (0)	E"
	536 (0)	E'

vw = very weak vs = very strong s = strong

ms = medium strong Relative intensities in brackets.

The mass spectrum of the solid (Table 3.3) was consistent with bromine being bound to C_2H_3N oligomers, and supported the microanalytical data in indicating a ratio for $Br:CH_3CN$ of 1:3. The origin of the peaks in the mass spectrum containing two bromine atoms is unclear, but the relative intensities of the peaks are small and some joining of monobrominated species may have occurred in the mass-spectrometer.

On the basis of the spectroscopic evidence and the analytical data, the solid was formulated as $[Br(C_6H_9N_3)][UF_6]$.

Variable Temperature $^{13}C\{^{1}H\}$ and ^{1}H NMR Spectra of $[Br(C_6H_9N_3)][UF_6]$ in CD_3CN or EtCN.

The $^{13}C\{^{1}H\}$ and ^{1}H NMR spectra of $[Br(C_6H_9N_3)][UF_6]$ in CD_3CN or EtCN contained broad signals at room temperature. The $^{13}C\{^{1}H\}$ spectrum of $[Br(C_6H_9N_3)][UF_6]$ at room temperature contained a very broad resonance at around 170 ppm. and two broad resonances between 20 and 35 ppm. In order to sharpen these signals, the solution was cooled to 193 K (Figure 3.2) In the spectrum recorded at 193 K six signals in the region δ_C = 22.3 to 27.8 ppm and two at δ_C = 31.6 and 32.4 ppm were observed. The region δ_C = 170.5 to 184.7 ppm contained nine singlets. The ^{1}H spectrum contained broad singlets at room temperature, on cooling to 193 K they sharpened and peaks at δ_H = 3.04, 3.25 and 4.88 ppm were observed, broad weak resonances were observed at δ_H 14.0 and 14.1 ppm.

From earlier spectroscopic evidence and analysis it was known that the compound contained a ring system consisting of C_2H_3N oligomers. This would be incompatible with the n.m.r spectrum, which contained too many signals for a simple ring system cation. To try to fit the earlier results with the n.m.r results, models were built to try to simulate a structure of a molecule having these spectroscopic properties. Isomers containing four membered rings or acyclic cations were considered, but the four membered ring systems were too strained to exist. 2,4,6-trimethyl, 1,3,5, triazine (Figure 3.3) was the compound with which the $[Br(C_6H_9N_3)][UF_6]$ compound was compared, its δ_C values are 175.9 C=N and 25.4 ppm (CH_3) respectively.[87] On the basis of this

NMR Spectrum of $[Br(C_6H_9N_3)][UF_6]$

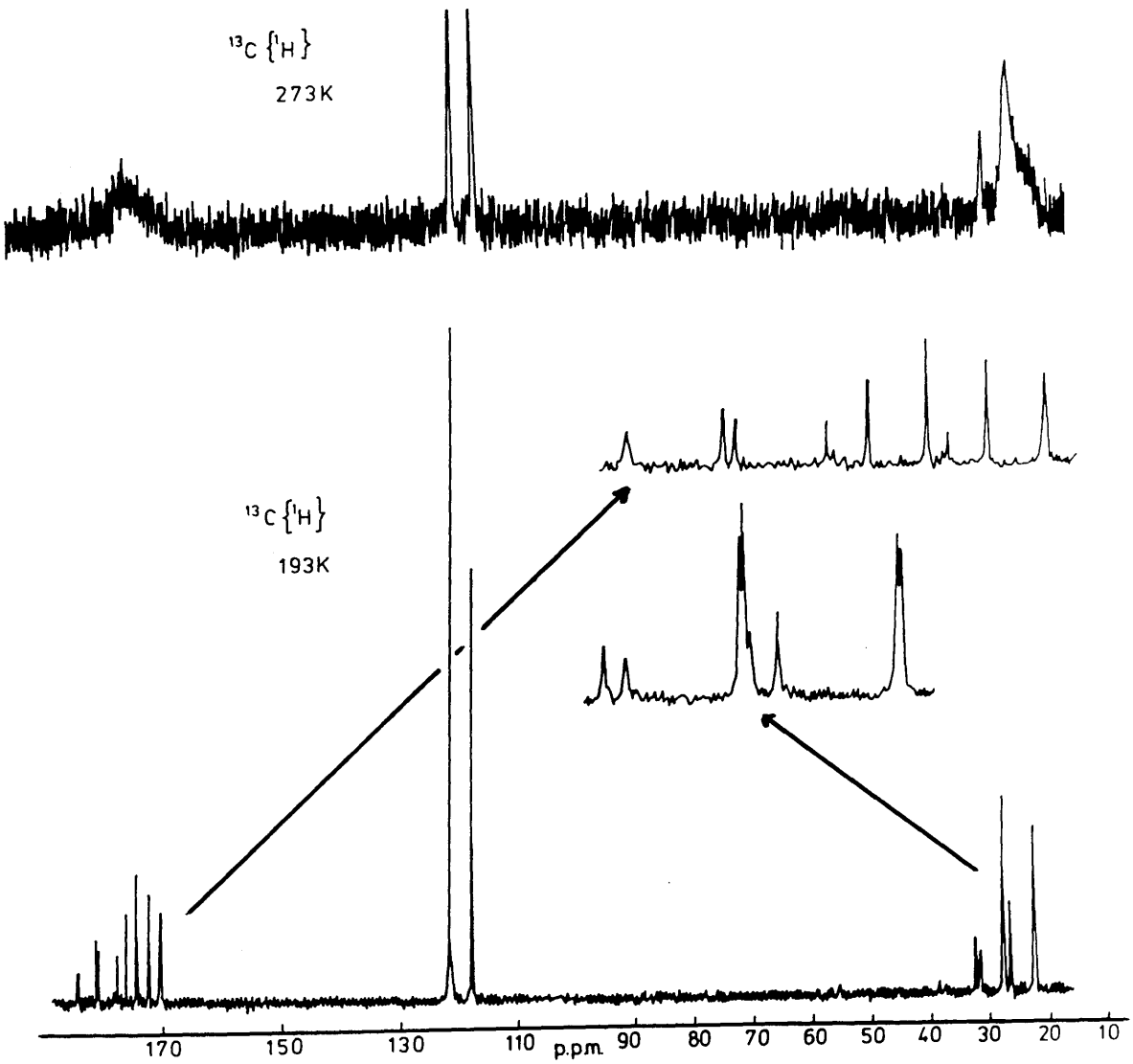
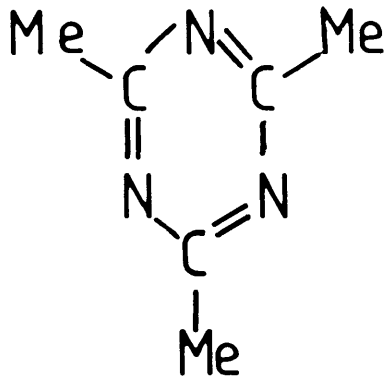


Figure 3.2



2,4,6-trimethyl,1,3,5 triazine

Figure 3.3

comparison the nine resonances between δ_C 170.5 to 184.7 ppm were assigned to C=N carbons having slightly different environments. The six signals in the region δ_C = 22.3 to 27.8 ppm and two at δ_C = 31.6 and 32.4 ppm were assigned to CH_3 and $-CH_2-$ groups respectively on the basis of DEPT experiments. The ^1H spectrum signals were assigned as follows δ_H; 3.04 and 3.25 ppm were assigned to CH_3 groups and δ_H 4.88 to $-CH_2-$ groups. The broad weak resonances at δ_H 14.0 and 14.1 ppm were assigned to NH protons.

The signals due to $-CH_2-$ and NH groups may have arisen from slight decomposition of the solid in the n.m.r. tube, catalysed by trace moisture. The absence of $-CH_2Br$ and NH groups in the vibrational spectra of $[Br(C_6H_9N_3)][UF_6]$ supports this.

Oxidations Involving $[Br(C_6H_9N_3)][UF_6]$ in MeCN.

Various oxidations involving $[Br(C_6H_9N_3)][UF_6]$ were attempted to determine the oxidation state of the bromine atom. The solvated copper cation $[Cu(NCMe)_4]^+$, NO (gas) and molecular iodine, I_2 were all reacted with $[Br(C_6H_9N_3)][UF_6]$ in MeCN at room temperature to determine the reaction stoichiometries. The products from the first two reactions are Br_2 and $[Cu(NCMe)_6]^{2+}$ or Br_2 and NO^+; material containing C=N groups is also present as a component of the product mixtures, confirmed by the appearance of bands in the infrared spectra of the products at ν_{max} 1620, 1565 and 1530 cm^{-1}. The appearance of the $[Cu(NCMe)_6]^{2+}$ cation was identified by electronic spectroscopy λ_{max} 775 nm [28], Br_2 being detected in the volatile material in each case by its electronic spectrum λ_{max} 418 nm.

$$[Br(C_6H_9N_3)][UF_6] + [Cu(NCMe)_4]^+ \xrightarrow{MeCN} \tfrac{1}{2}Br_2 + [Cu(NCMe)_6]^{2+} \quad (5)$$

$$NO(g) + [Br(C_6H_9N_3)][UF_6] \xrightarrow{MeCN} NO^+ + \tfrac{1}{2}Br_2 \quad (6)$$

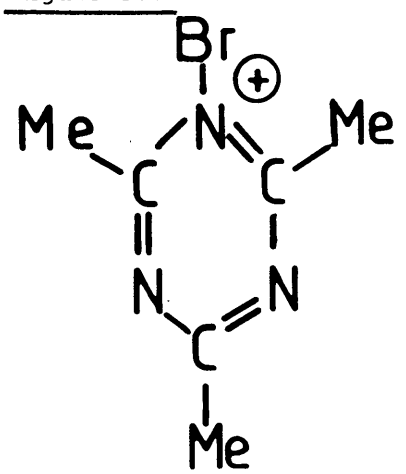
Several aliquots of a standard iodine solution were reacted with differing amounts of $[Br(C_6H_9N_3)][UF_6]$ in MeCN. The absorbance of I_2 at λ_{max} 460 nm was monitored, then the $[Br(C_6H_9N_3)][UF_6]$ was added. A shift in the band position to ca 400 nm due to Br_2 formation occurred. The product from the oxidation of I_2 is not $[I(NCMe)_2]^+$ but appears to contain iodine bound to an MeCN oligomer analogous to $[Br(C_6H_9N_3)][UF_6]$. This is consistent with the presence of C=N groups and $(UF_6)^-$ in its infrared spectrum and major peaks (m/z) in its mass spectrum at 249 $C_6H_8IN_3$ (24.4), 168 C_2H_3IN (3.9)

167 C_2H_2I (8.5) assigned to iodine bound to C_2H_3N oligomers, (relative intensities in brackets). This product decomposed readily to give I_2 in solution even at low temperatures, this precluded detailed examinations.

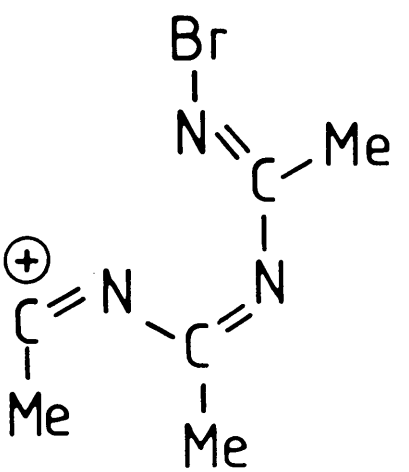
Discussion of the Oxidation of Bromine by Uranium Hexafluoride in Acetonitrile.

The oxidation of molecular bromine in MeCN differs from that of molecular iodine under similar conditions in two respects. Firstly oxidation occurs only with the thermodynamically stronger oxidising agent UF_6 ; and secondly the cation formed cannot be described simply as $Br(NCMe)_2^+$. From the evidence in the results section the species contains the UF_6^- anion; it has an electrophilic bromine cation with the empirical formula $[Br(C_6H_9N_3)]^+$. To suggest a structure for the cation, a reaction scheme and mechanism by which it could be formed has to be postulated. In order to account for the temperature dependent n.m.r. spectra it is necessary to postulate the existence in solution of an equilibrium between cyclic and acyclic forms of the cation

Figure 3.4.



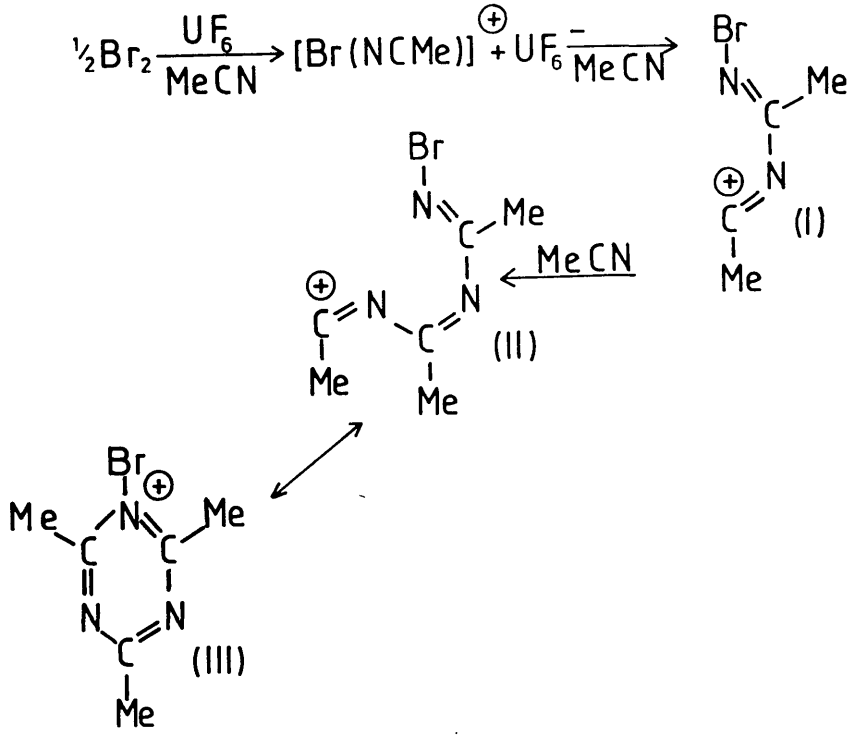
CYCLIC



ACYCLIC

The acyclic form of the cation is capable of existing in several conformations for example planar, syn or anti with respect to the central C=N bond. By constructing this model and considering the restricted rotation about the central C=N bond a number of preferred configurations could be visualised. These configurations which have a slightly different chemical environment could account for the complex set of nine signals in the $^{13}C\{^{1}H\}$ n.m.r. spectrum observed at 193 K. (Figure 3.2). Other explanations for example, the formation of species with $\overline{C = N - C = N}$ four membered rings are possible but are less attractive. From model building there appears to be too much strain on a four membered system containing two double bonds which favours the six membered ring system.

A possible structure for the cation and the pathway by which it could be formed are given in Scheme 3.2.

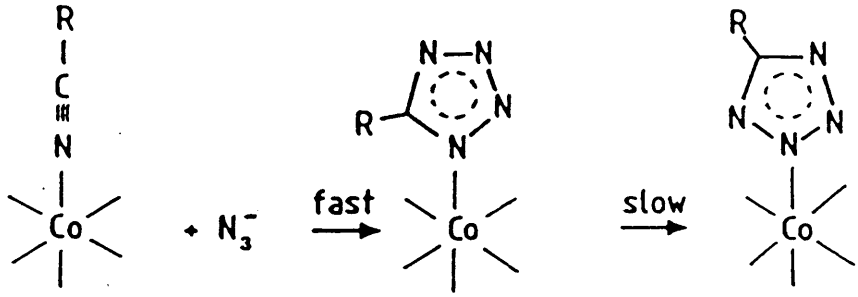


Scheme 3.2

It appears that Br^+ is too electrophilic to exist as a simple cation solvated by the relatively weak ligand MeCN, and oligomerisation of MeCN occurs to give species represented by (I) and (II) in the Scheme 3.2. The isolation of a salt containing the $[Br(C_6H_9N_3)]^+$ cation is rationalised by the ring closure of (II) to give the cation (III) in which the positive charge would be expected to be delocalised.

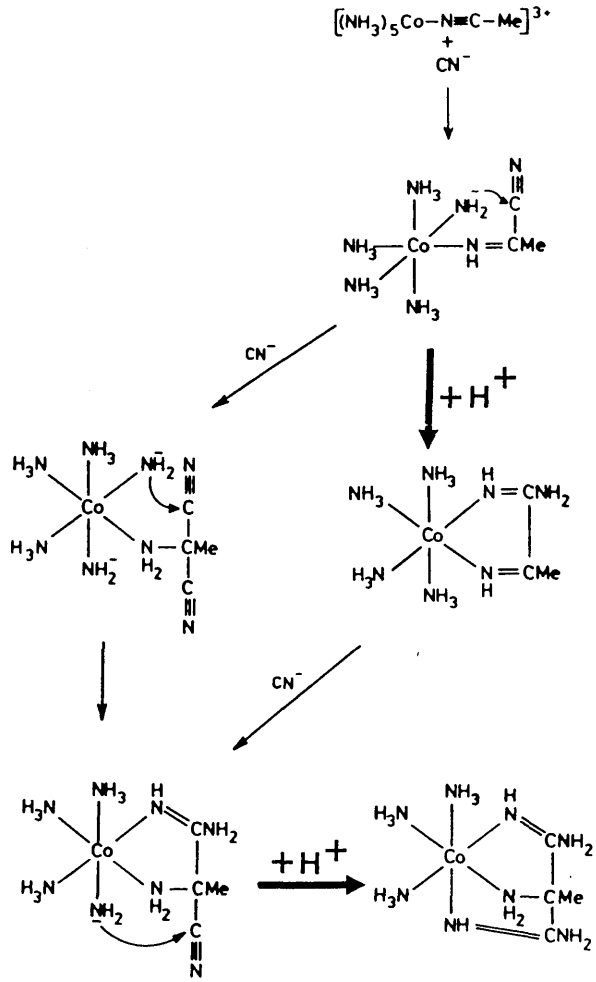
Coordination compounds with organonitrile ligands are of considerable interest due to the increased susceptibility of the coordinated nitrile to nucleophilic attack by reagents such as the hydroxide ion. Nucleophilic attack at the cyano carbon of an organic nitrile is enhanced greatly by coordination of the cyano carbon to an electrophilic centre. For example the hydrolysis of MeCN to acetamide in aqueous base is 2×10^6 faster for coordinated MeCN in the complex $[(H_3N)_5Co(NCMe)]^{3+}$ than it is for free MeCN.[88] Particular attention has been directed towards comparisons of ligand properties and reactions between different organonitrile complexes of the general type $M(H_3N)_5(RCN)^{n+}$ where M = Ru(II), Ru(III), Rh(III) or Co(III) and RCN is an organonitrile such as acetonitrile or benzonitrile.

Nucleophilic attack has also been exploited for synthesis, for example in the formation of 5-methyl tetrazole by nucleophilic attack of N_3^- on $[(H_3N)_5Co(NCMe)]^{3+}$ according to the equation 7.[89]



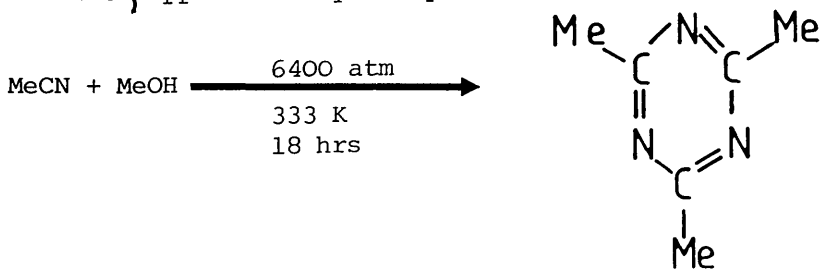
7

The formation of 5-methyl tetrazole from sodium azide and acetonitrile requires a reaction time of 25 hours at 423 K compared with only 2 hours at ambient temperature for coordinated acetonitrile. Also in the preparation of a tridentate bis (amidine) aminomethyl malonate chelate complex[90] initiated by nucleophilic attack of CN^- on $[(H_3N)_5Co(NCMe)]^{3+}$ at the nitrile carbon atom and addition of another CN^- with two intramolecular condensations involving bound amide ions yields the complex (Scheme 3.3).



Scheme 3.3

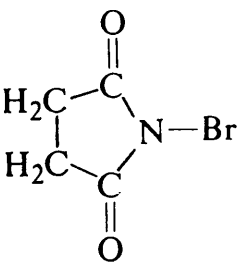
The reaction pathway postulated in this work is directly analogous with Br^+ acting as the electrophilic centre for nitrile coordination. This could account for the ease of nitrile oligomerisation, to give the triazine type cation. Nitriles are generally trimerised to s-triazines under very high pressures and temperatures for example[91], equation 8, approximately 40% yield.



(8)

If the reaction conditions are not carefully controlled, or if the reaction is carried out in EtCN, polymerisation of the solvent is more extensive and a well defined product is not isolated. This situation is similar to that encountered previously in reactions between binary fluorides and Cu^{I} trimethyl phosphite complexes in MeCN where solvent polymerisation occurs, apparently initiated by the CH_3^+ cation.[92] It is suggested that $[CD_3CNMe]^+$ is formed which initiates polymerisation of the solvent. The cation was not identified, but MeCN is known to behave as a trap for carbocations, for example, R_3C^+ reacts with MeCN to give $[R_3CNCMe]^+$ which is subsequently hydrolysed to $R_3CN(H)C(O)Me$[93] and $[MeCNMe^+][O_3SCF_3^-]$ has been isolated from the reaction of $MeOSO_2CF_3$ with MeCN.[94]

The structures proposed for the cation $[Br(C_6H_9N_3)]^+$ are unusual but its chemical behaviour is not dissimilar from those of other N-Bromo compounds, for example, N-Bromo succinimide,[95] which contains electrophilic bromine.



N-Bromosuccinimide
(NBS)

The species formed by the anodic oxidation of Br_2 in MeCN has been suggested to be $[Br(NCMe)_n][Br_3]$ n = 1, or 2. The anion was identified by its electronic spectrum but no direct evidence for the cations structure was presented.[79] The brominating properties of the cation could be accounted for equally well by the structure

suggested in this work. The brominating properties of $[Br(C_6H_9N_3)]^+$ will be discussed in Chapter 6.

EXPERIMENTAL

Unless described below, procedures for purification of reagents, manipulation of products, and spectroscopic measurements were as described in Chapter 7.

Bromine (B.D.H. AnalaR) was degassed and dried over P_2O_5, then vacuum distilled three times over fresh P_2O_5. Mass spectra were obtained using a Kratos MS12 spectrometer, with direct injection of sample, and electron bombardment ionisation. ^1H and $^{13}C\{^1H\}$ n.m.r spectra were obtained using a Bruker WP200JY at 200 (^1H) or 50 MHz (^{13}C). Chemical shifts (δ p.p.m) are reported with respect to CD_3CN at δ_C 1.3 and CHD_2CN at δ_H 1.93 and are positive to higher frequency.

Preparation of $[Br(C_6H_9N_3)][UF_6]$

A solution of Br_2 (2.0 mmol) in MeCN (5 cm^3) was prepared *in vacuo* and UF_6 (*ca* 0.7 mmol) added to the frozen solution by vacuum distillation in a double limbed vessel. On warming the mixture to room temperature its dark red colour changed to a pale red. Removal of volatile material by back distillation left a pale green solid.

Analysis : Found C, 12.9; H, 1.7; Br, 14.5; F, 20.3; N, 7.4; U, 43.1% $C_6H_9BrF_6N_3U$ requires. C, 13.0; H, 1.6; Br, 14.4; F, 20.5; N, 7.5; U, 42.9%.

Its vibrational spectra are listed in Table 3.2 and its electronic spectrum in MeCN is tabulated in Table 3.1.

Reaction of Br_2 with UF_6 in Propionitrile (EtCN).

A solution of Br_2 (2.0 mmol) in EtCN (5 cm^3) was prepared *in vacuo* and UF_6 (*ca* 0.7 mmol) added to the frozen solution. On warming the mixture to room temperature its dark red colour changed to paler red. When the volatiles were being removed the solution changed from pale red to green, eventually an oily green liquid was obtained which would not solidify. The oil was pumped overnight, there appeared to be some solid in the oil, but this could not be separated, which made spectroscopic examination difficult. Its electronic spectrum in MeCN showed bands due to UF_5, and UF_6^-.

Reaction of Br_2 with MoF_6 in Acetonitrile.

A solution of Br_2 (2.0 mmol) in MeCN (5 cm^3) was prepared *in vacuo*, MoF_6 was added in various stoichiometric amounts ranging from 0.7 mmol - 2.0 mmol. After the solutions had stood at room temperature for 4 hours the volatiles were removed; no product was isolated.

Reactions of $[Br(C_6H_9N_3)][UF_6]$ in MeCN.

(i) With Nitric Oxide (NO)

Excess NO gas was allowed to react with a mixture of $[Br(C_6H_9N_3)][UF_6]$ (0.54 mmol) in MeCN (5 cm^3). Br_2, identified by its electronic spectrum λ_{max} = 390 nm, was immediately liberated. Removal of the volatile material left a pale green solid (0.265g). For complete reaction to $NOUF_6 + C_6H_9N_3$, the mass of product required would be 0.273g. The infrared spectrum of the solid contained bands due to NO^+, $\nu(NO)$ = 2330 cm^{-1}.[96] UF_6^-, ν_3 = 520 cm^{-1},[35] and at 1620, 1575 and 1520 cm^{-1} assigned to ν (C=N).

(ii) With tetrakis(acetonitrile)copper(1)hexafluorophosphate.

$[Br(C_6H_9N_3)][UF_6]$ (0.18 mmol), contained in a frangible Pyrex ampoule, was added to $[Cu(NCMe)_4][PF_6]$[61] (0.18 mmol) and MeCN (5 cm^3) in an evacuable Spectrosil cell. The frangible ampoule enabled the electronic spectrum of the solution to be recorded before and after oxidation had occurred. The ampoule was broken by shaking the cell, this allowed the $[Br(C_6H_9N_3)][UF_6]$ complex to react with the Cu^I salt. The spectrum of the resulting solution was recorded, and $[Cu^{II}]$ was determined as 0.0375 mol dm^{-3} (required for complete oxidation of Cu^I 0.036 mol dm^{-3}). A similar reaction using an excess of the Cu^I salt yielded a blue-green solid whose i.r. spectrum contained bands assigned to coordinated MeCN,[97] PF_6^-,[98] UF_6^- [84] and bands at ν_{max} 1620, 1565 and 1530 cm^{-1} assigned to C=N- groups.[86] Br_2 was detected in the volatile fraction.

(iii) With Molecular Iodine.

Aliquots (5,0 cm^3) of a standard solution of I_2 in MeCN (2.13×10^{-3} mol dm^{-3}) were transferred in a glove box to dried, evacuable Spectrosil cells and weighed portions of $[Br(C_6H_9N_3)][UF_6]$ ($4.8 - 0.95 \times 10^{-5}$ mol) contained in frangible glass ampoules were added. Absorbances of I_2 at 460 nm were determined, the ampoules broken and the spectra of the products obtained. In most solutions λ_{max} shifted to ca. 400 nm due to Br_2 formation but in the reaction where the bromine salt was 0.95×10^{-5} mol, I_2 unreacted was estimated as 0.65×10^{-5} mol (expected for complete reaction 0.59×10^{-5} mol). A mixture of I_2 (0.2 mmol) and $[Br(C_6H_9N_3)][UF_6]$ (0.2 mmol) in MeCN (5 cm^3) was allowed to react at room temperature and gave a pale brown solid after removal of unreacted I_2, Br_2 and MeCN. Its i.r. spectrum was similar to that of $[Br(C_6H_9N_3)][UF_6]$ containing bands 515 cm^{-1} assigned to $[UF_6]^-$ [84] and at 1620, 1575 and 1510 cm^{-1} assigned to ν (C=N). Major peaks (M/Z) in its mass spectrum with their assignments were 249, $C_6H_8IN_3^+$ (26.4); 168, $C_2H_3IN^+$ (3.9); 167, $C_2H_2I^+$ (8.5); 166, C_2HIN^+ (2.9), and 127 I^+ (22.3), (relative intensities in brackets).

The solid decomposed readily at room temperature giving I_2 as one product.

Its $^{13}C\{^1H\}$ n.m.r. spectrum in CD_3CN contained signals at δ_C = 28.9 and 28.7 p.p.m assigned to CH_3- groups.

CHAPTER 4

REACTIONS BETWEEN CHLORINE OR HYDROGEN CHLORIDE AND URANIUM HEXAFLUORIDE IN ACETONITRILE.

INTRODUCTION

As was stated in the introductory chapter, there is no evidence for Cl^+ or Cl_2^+ in superacid media.[2] It is possible however that in the basic, coordinating solvent MeCN a chlorine cation might be stabilised through coordination to MeCN. This hypothesis has been tested and the results are described in this chapter. The ease of oxidation of the halogens increases down the group, so it was predicted that chlorine would prove more difficult to oxidise than iodine or bromine although the methods employed to oxidise these elements are an obvious route. This prediction proved to be correct and although it appears that no simple $[Cl(NCMe)_x]^+$ cationic species were formed, interesting reactions occurred.

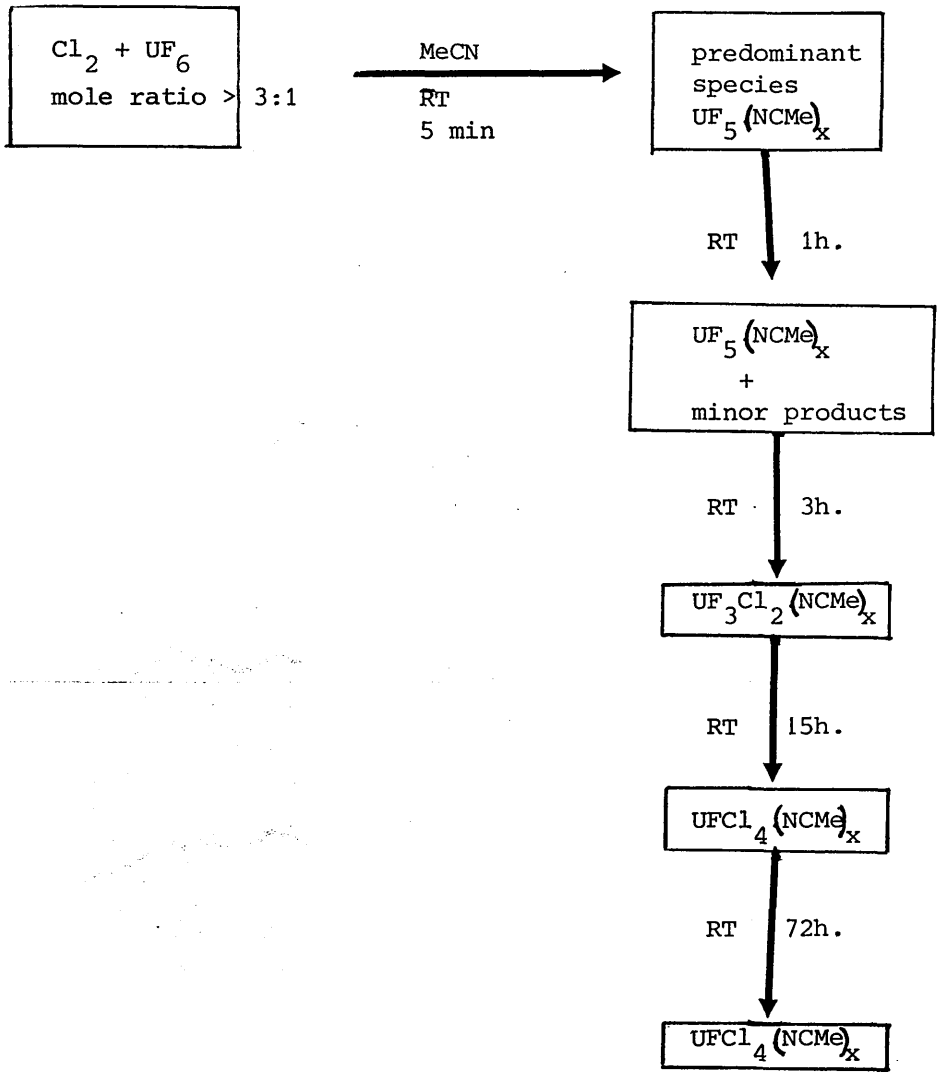
When Cl_2 and UF_6 were mixed in MeCN, uranium pentafluoride was formed which subsequently underwent halogen exchange to give a mixture of chloridefluorides of uranium(V). It has been shown in previous work that Cl_2 in MeCN gives HCl as one product after several hours reaction.[99] The reaction of HCl with UF_6 in MeCN was therefore studied also, in the hope that it would elucidate the reaction pathway of the reaction of Cl_2 with UF_6 particularly in its later stages.

Reaction of Chlorine with Uranium Hexafluoride in Acetonitrile.

Addition of uranium hexafluoride to a frozen solution of molecular chlorine in acetonitrile mole ratio Cl_2:UF_6 > 3:1, results in the formation of a lime green solution as the mixture warms to room temperature. Removal of unreacted Cl_2 and MeCN leads to the precipitation of numerous products which varied in composition depending on the exact conditions used. Attempts were made to obtain a single reproducible product, but due to the complexity of the reaction a mixture of products was always obtained. The mixture of Cl_2 and UF_6 in MeCN was reacted for varying times and during isolation of the product the solution was kept at low temperatures, but no single product was obtained. The electronic spectra of reaction mixtures were recorded at various times after mixing and these gave complex spectra indicating halogen exchange was occurring. The adduct $UF_5(NCMe)_x$ was the initial product observed. The flow diagram (Diagram 4.1) shows the appearance of products from a reaction mixture with time, the spectra are shown in Figure 4.2.

The vibrational spectra of products isolated varied according to the isolation method and temperature. Bands consistent with the presence of the groups NH, C≡N, C=N, CH_3, C-C, and bands characteristic of $[UF_6]^-$ and $UF_5(NCMe)_x$ were found for most reactions. Appearances of the solids, the methods used for their isolation, the temperature at which they were isolated, and their spectroscopic results are summarised in Tables 4.3 to 4.9.

Diagram 4.1



Products identified in MeCN solution with time from reaction of Cl_2 with UF_6 in MeCN at room temperature.

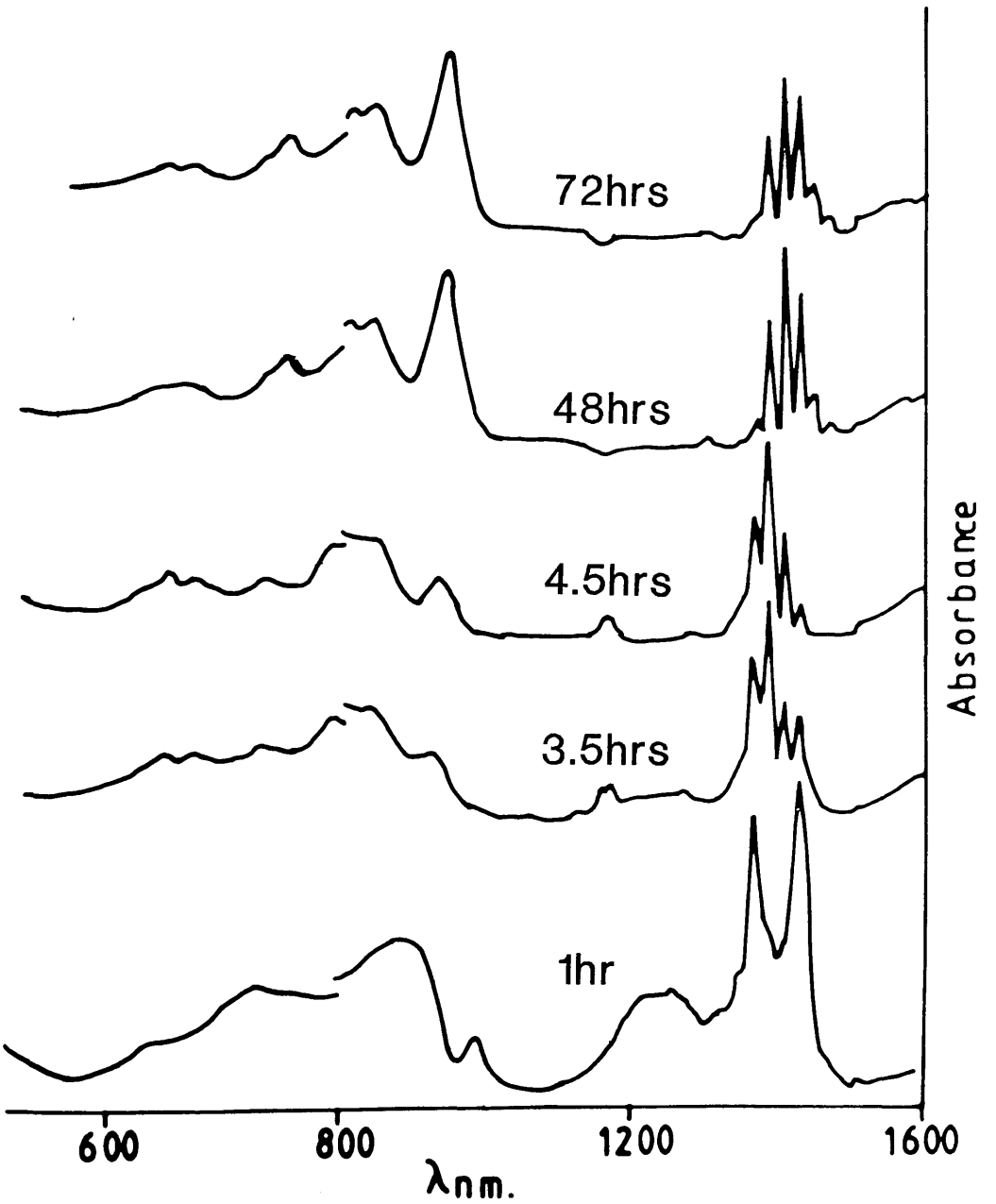

Cl_2+ UF_6 in MeCN
72hrs
48hrs
4.5hrs
3.5hrs
1hr
Absorbance
600
800
1200
1600
λnm.

Figure 4.2

TABLE 4.3

Vibrational spectrum of product* from Chlorine and Uranium Hexafluoride in Acetonitrile isolated at room temperature.

I.r. cm^{-1}	Assignment
2324) 2312) 2283)	CH_3 def + CC str(A_1) CN str.(A_1)
1037	CH_3 rock
968	
950	
935	C-C str
720	
600-500 vs	$[UF_6]^-$, UF_5.

*This solution stayed green during isolation and a green/brown solid was obtained. Its electronic spectrum in MeCN is shown in Figure 4.3a.

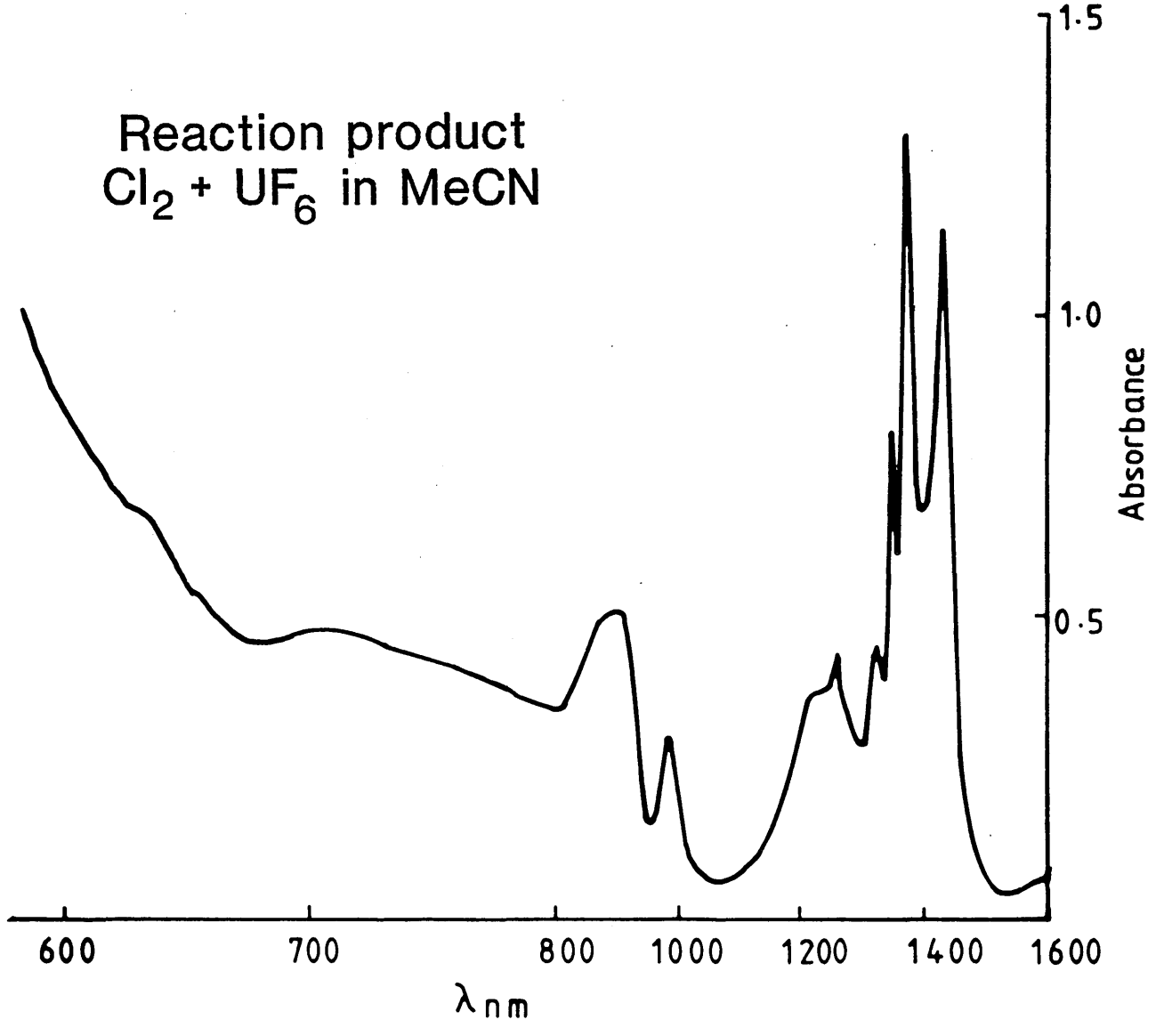

Reaction product
Cl_2 + UF_6 in MeCN
1·5
1·0
0·5
Absorbance
600
700
800
1000
1200
1400
1600
λ nm

Figure 4.3a

TABLE 4.4

Vibrational spectrum of product* from Chlorine and Uranium Hexafluoride in Acetonitrile isolated at 273 K.

I.r. cm^{-1}	Assignment
3300-3100	NH
2305 2280	C≡N str.
1700	C=O ?
1620	C=N str
1035	CH_3 rock
955	C-C str
828	
720	
518	$\nu_3[UF_6]^-$

*This solution stayed green during isolation and a dark green product was obtained.

TABLE 4.5

Vibrational spectrum of product* from Chlorine and Uranium Hexafluoride in Acetonitrile isolated at 273 K.

I.r. cm^{-1}	Assignment
2315 2285	C≡N
1155	
1040	CH_3 rock
965	C-C
938	
722	
519	$\nu_3[UF_6]^-$

*The solution stayed green during isolation but brown flakes were found in the green solid isolated.

TABLE 4.6

Vibrational spectrum of product* from Chlorine and Uranium Hexafluoride in Acetonitrile after 18 hours at Room Temperature.

I.r. cm^{-1}	Assignments	I.r. cm^{-1}	Assignments
3300 vb 3100 vb	NH str	1020 m	
2300 m	CH_3def+C-C str	1005 m	
2265 m	C≡N str	988 s	C-C str
1690 s		975 s	
1605 s	C=N str	830 s	
1545 s	C=N str	790 s	
1340 s	CH_3 def	715 s	
1165 m		695 s	
1040 m	CH_3 rock	600 m	
		580 m	
		520 s	$\nu_3[UF_6]^-$
		505 s	
		440 m	

*This product was brown in colour and oily.

TABLE 4.7

Mass spectrum of white material obtained from product in Table 4.6

M/Z	int	Assignment	M/Z	int	Assignment
47	35.3	$[CCl]^+$	258	31.0	
49	13.0		260	42.4	a*
73	32.6	$[CClCN]^+$	262	20.7	
75	12.0		264	4.9	
82	31.5				
84	27.2	$[CCl_2]^+$			
86	5.4		292	50.5	
108	100.		294	76.6	
110	62.5	$[CCl_2CN]^+$	296	44.0	b*
112	13.0		298	16.3	
117	21.2		300	1.1	
119	22.3	$[CCl_3]^+$			
121	8.2				
123	2.2				
134	17.4				
136	12.	$[Cl_2C(CN)_2]^+$			
138	2.7				

Theoretical splitting patterns

1 Cl	3:1
2 Cl	9:6:1
3 Cl	27:27:9:1
4 Cl	81:108:54:12:1

* Definitive assignments cannot be made for a and b but the intensities and splitting patterns are close to that required for 3 and 4 Cl atoms respectively.

TABLE 4.8

Preparation for nmr analysis of product from Chlorine and Uranium Hexafluoride in Acetonitrile.

$^{13}C\ \{^{1}H\}$ nmr spectrum at 295 K.

δ_C ppm	intensity	Assignment
26.4	5	CH_3
29.2	8.8	CH_2
116.2	2.5	C≡N
187.3	1.5	C=N

^{1}H nmr spectrum

δ_H ppm	intensity	Assignment
2.86	17.3	CH_3
4.2	9.0	CH_2 *
10.8	0.9	NH
11.1	1.25	
11.4	0.95	

*DEPT Measurements.

TABLE 4.9

Vibrational spectrum of product* from Chlorine and Uranium Hexafluoride in Acetonitrile one hour reaction.

I.r. cm^{-1}	Assignment.
3300 vb	NH
3100 vb	NH
2315 m	CH_3def+C-C str
2285 m	C≡N
1680 s	
1610 s	C=N str
1540 s	C=N str
1385 m	CH_3def
1295 m	
1040 m	CH_3 rock
1030 m	CH_3 rock
980 s	
920 s	C-C
720 s	
695 s	
605 m	
600 m	
515 vs	$\nu_3[UF_6]^-$

*Solution stayed green during isolation, green product obtained.

To enable comparisons to be made, work done on β-UF_5 in acetonitrile, and uranium(V) chloridefluoride formation was considered. A pale green solution is obtained when β-UF_5 is dissolved in MeCN which is stable to disproportionation. Removal of the solvent results in the precipitation of a 1:1 adduct UF_5.NCMe.[100] Raman spectra of the solid complex and the solution are identical and consist of bands at 602 and 611 cm^{-1} (both polarised in MeCN). The solids i.r. spectrum contains bands characteristic of coordinated MeCN, and strong bands at 530 and 350 cm^{-1}. The electronic spectrum of UF_5 in MeCN consists of four groups of bands and is similar to that of $[UF_6]^-$, but there are sufficient differences in band positions and in the associated vibronic structure to enable the two species to be distinguished. The symmetry of UF_5 as an isolated molecule is not known[101] but it is believed to be C_{4v}.[102] Although the presence of polymeric species in MeCN cannot be ruled out, the electronic spectrum favours monomeric UF_5.NCMe in which distortion from O_h symmetry at U^V is small.

In contrast to the above formulation Halstead *et al*[103] favoured a salt formulation for UF_5 in MeCN, giving $[UF_4(NCMe)_x][UF_6]$ in acetonitrile solution, on the basis of the following observations.

1. UF_5 in MeCN has a molar conductance (140 and 170 Ω^{-1} cm^2 mol^{-1} at 2.2×10^{3} and 1.3×10^{-3} M concentrations based on UF_6^-) indicating a 1:1 conductor.
2. In the electronic spectrum sharp bands are observed at 1323 and 1351 nm corresponding to components of the $\Gamma 7 - \Gamma 7'$ transition which is highly characteristic of the UF_6^- anion. Much stronger bands overlap this region and also occur near

1250 and 833 nm, these absorptions are assigned to a less symmetric solvated UF_4^+ cation.

3. A broad (1100 G) single line EPR signal is observed in frozen MeCN at $|g|$ = 0.759. This g value is in the region characteristic of the octahedral UF_6^- anion.[104] However an EPR signal was not observed for solid UF_5.NCMe. The authors were unable to say whether this effect was due to relaxation caused by distortion of UF_6^- in the less highly solvated environment[105] or whether a significantly different structure is present in the solid.

The stepwise chlorination of UF_5 in MeCN by Me_3SiCl or UCl_5 yields soluble uranium(V) chloridefluorides.[106] The electronic spectra of the UF_5, Me_3SiCl mixtures in the mole ratio 1:1 to 1:5 have been recorded and the 1:5 spectrum is virtually identical to UCl_5.2NCMe.[107] Intermediate spectra all differ from one another and they are also different from UF_5 and UCl_5 in MeCN. The spectra of the mixtures contain similarities for example, the spectrum of the 1:1 ratio appears to be a composite of those of the 1:2 ratio and UF_5 in MeCN having no unique peaks of its own. It is not apparent whether the solutions contain individual spectra for example, $UClF_4(NCMe)_x$ or mixtures such as $UF_5(NCMe)_x$ and $UCl_2F_3(NCMe)_x$.

To obtain crystalline solids from the above mixtures the ligand triphenylphosphine oxide (tppo) was added. Addition of tppo (2-3 equivalents) to a solution of UF_5 in MeCN resulted in the precipitation of UF_5.2tppo. Addition of 2 equivalents of tppo to the MeCN solution "U Cl_2 F_3" gave a bright yellow precipitate identified as UCl_2F_3.2tppo. This preliminary account of the work was available prior to the present work described in this thesis, and a more

complete account[108] appeared while the present work was in progress. This detailed the preparation and some properties of the complete series of compounds $UCl_xF_{5-x}.nMeCN$ ($0 \leqslant x \leqslant 5$, n = 1 and 2) and $UCl_xF_{5-x}.ntppo$ ($0 \leqslant x \leqslant 5$, n = 1 and 2).

Reaction of Anhydrous Hydrogen Chloride with Uranium Hexafluoride in Acetonitrile at Room Temperature.

Addition of UF_6 to a frozen solution of HCl in MeCN mole ratio $HCl:UF_6$ > 8:1 gave a green solution as the mixture was allowed to warm to room temperature. The electronic spectrum of the solution recorded immediately after warming to room temperature (Figure 4.3) resembled the spectrum assigned to $UFCl_4(NCMe)_x$ which was obtained after 15 hours from the reaction between Cl_2 and UF_6 in MeCN.

By adding tppo to the solution of HCl and UF_6 in MeCN by analogy with the work by Holloway et al, a product would maybe crystallise out of solution. Removal of the volatile material from a mixture of HCl, UF_6 and tppo in MeCN, left a green solid shown to be UF_5.tppo by its electronic spectrum (Fig 4.4) and infrared spectrum (Table 4.10). When tppo was added to a mixture of HCl and UF_5 in MeCN that had been allowed to react for several hours, a sticky light yellow solid was obtained, that remained sticky after pumping for several hours. This was presumably due to unremoved solvent; the difficulty in removing last traces of solvent was also experienced by Holloway et al.[108] The more chlorinated their compounds the more yellow was the product isolated and the more

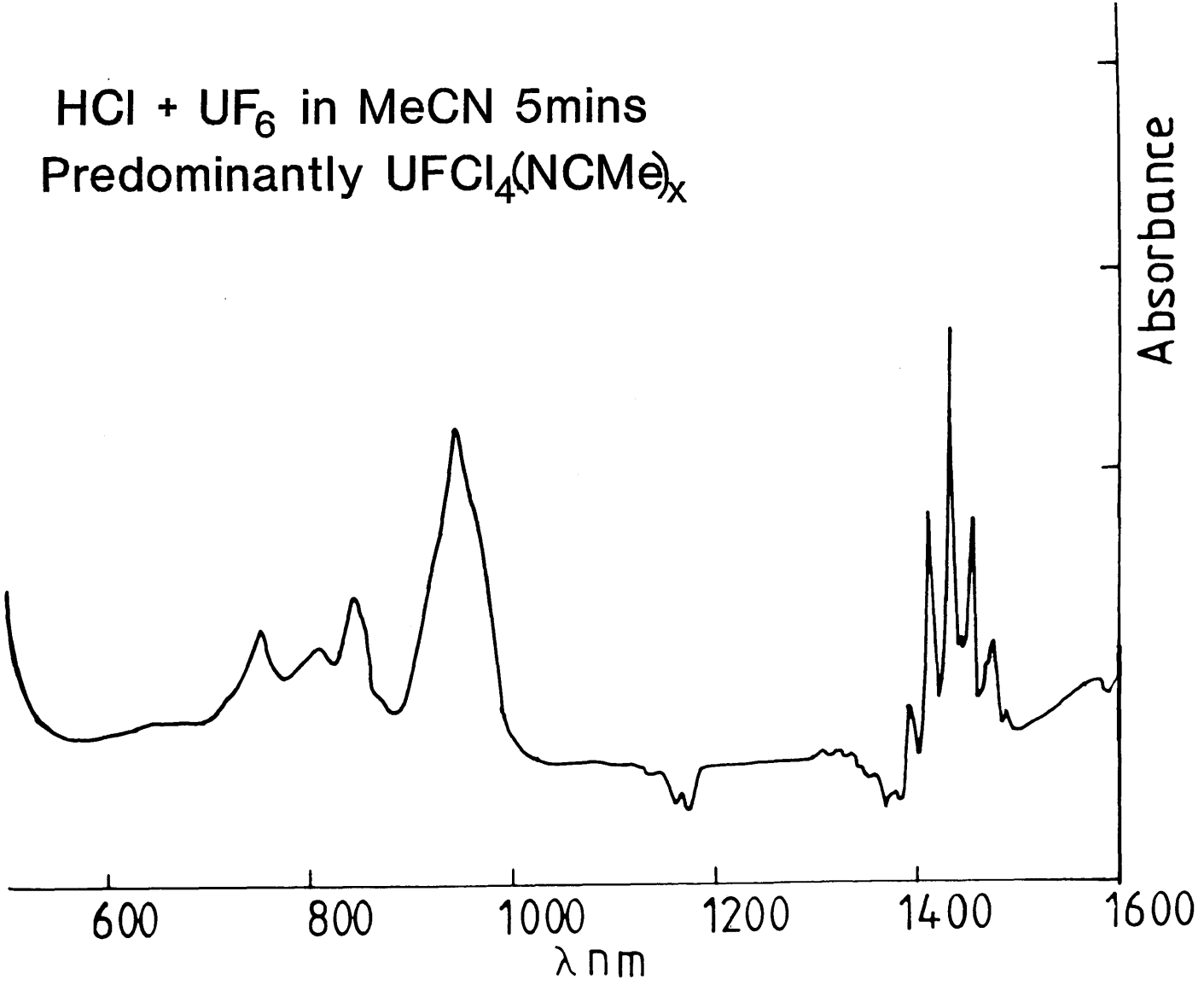

HCl + UF6 in MeCN 5mins
Predominantly UFCl4(NCMe)x
Absorbance
600
800
1000
1200
1400
1600
λ nm

Figure 4.3

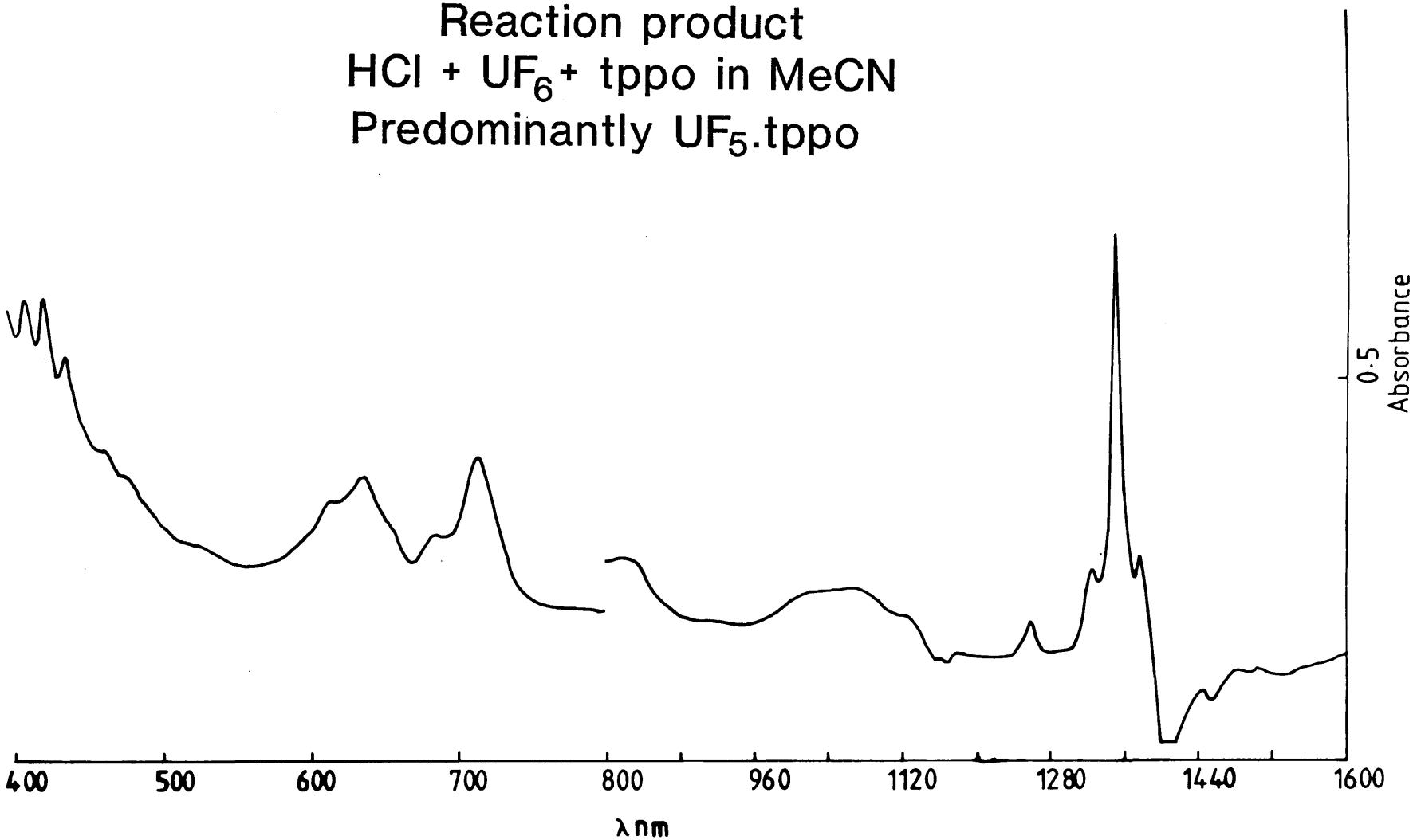

Reaction product
HCl + UF6+ tppo in MeCN
Predominantly UF5.tppo
0.5
Absorbance
400
500
600
700
800
960
1120
1280
1440
1600
λnm

Figure 4.4

TABLE 4.10

IR spectrum of the adduct formed between Hydrogen Chloride, Uranium Hexafluoride and Triphenylphosphine oxide in Acetonitrile.

Product	Assignment	UF_5.tppo
1485 s	ν C-C	1482 w
1435 m	ν C-C	1433 m
1338 s	comb	
1312 m		
1248 m		
1185 m	P=O	
1162 m		
1120 s	β C-H	1120 s
1060 s	β C-H	1075 wbr
1025 m	β C-H	1044 s
995 m	ring	1022 m 997 m
950-820 vb		
750 m	ζ C-H	758 sh
730 s	ζ C-H	751 s
690 vs	∅ C-C	728 vs
615 m		689 vs
590 s	ν U-F	602 s
540 vs	ν U-F	539 vs
490 m		529 vs
450 m		508 s
		449 w

difficult it became to isolate crystalline. Redissolving the sticky product from HCl, UF_6 and tppo in MeCN gave an electronic spectrum resembling $UFCl_4$.tppo, (Figure 4.7). An infrared spectrum was recorded but was unsatisfactory due to the difficulties in obtaining a Nujol mull.

Discussion of the Reactions Between Cl_2 and UF_6 in MeCN and HCl and UF_6 in MeCN.

The reaction of Cl_2 and UF_6 in MeCN is not as straightforward as the analogous reactions involving Br_2 and I_2. Uranium(V) pentafluoride is formed in solution immediately, then halogen exchange occurs giving mixtures of uranium(V) chloridefluorides. The reaction appears to stop at the $UFCl_4(NCMe)_x$ species and even after the reaction is allowed to continue for a few days the $UFCl_4(NCMe)_x$ species predominates. The halogen exchange process takes several hours with approximately 15h being required for $UFCl_4(NCMe)_x$ to be the major species in solution.

The reaction between HCl and UF_6 in MeCN produces $UFCl_4(NCMe)_x$ in the time of mixing. This observation suggests that HCl is the active species in the chlorine/UF_6 system and that the rate determining step of the chlorine/UF_6 reaction is the formation of HCl which subsequently undergoes a reaction with the $UF_5(NCMe)_x$ adduct giving halogen exchanged products.

It has been shown that $UF_5(NCMe)_x$ undergoes halogen exchange with Me_3SiCl or UCl_5 [106] in acetonitrile to yield soluble uranium(V)

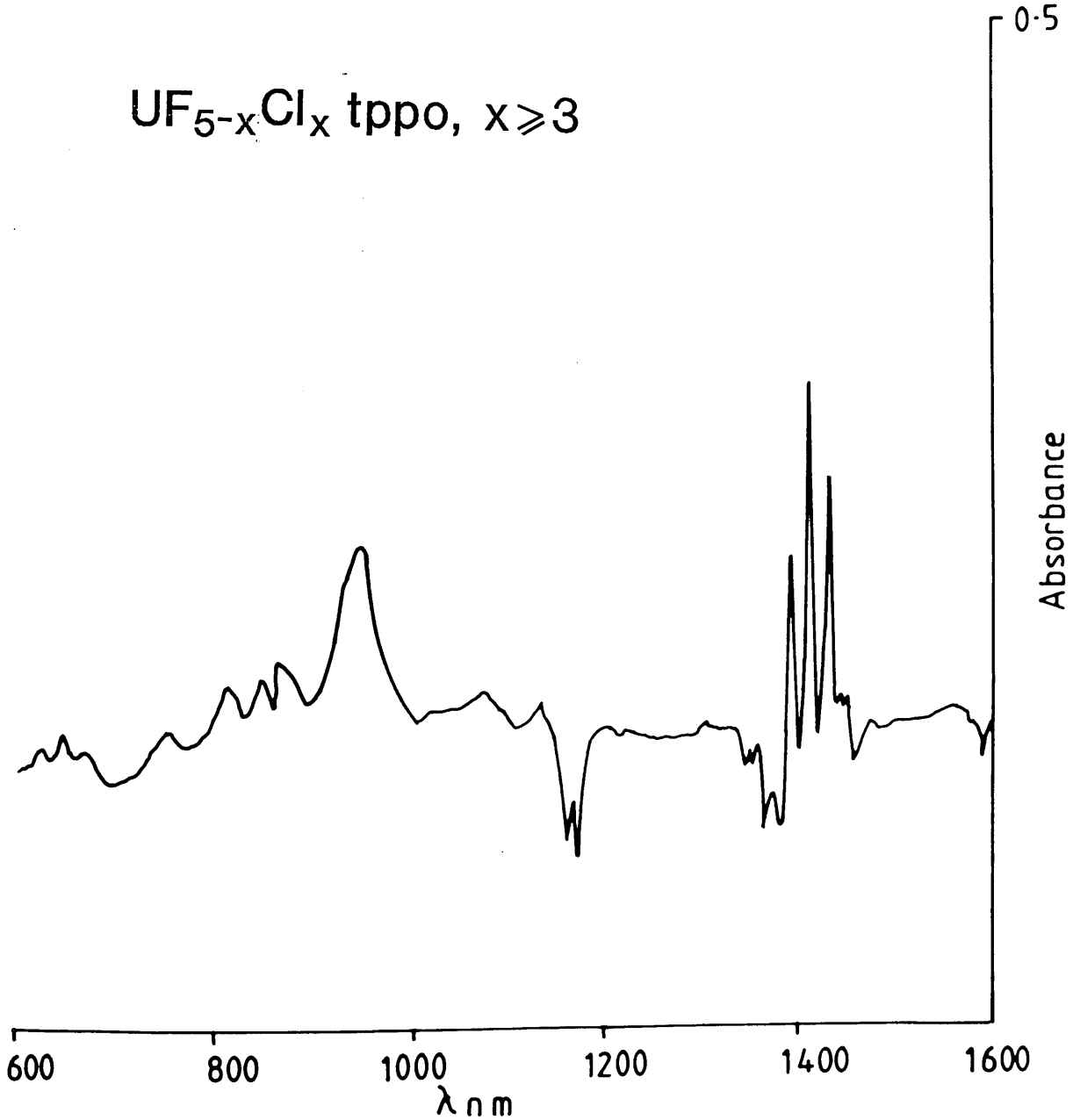
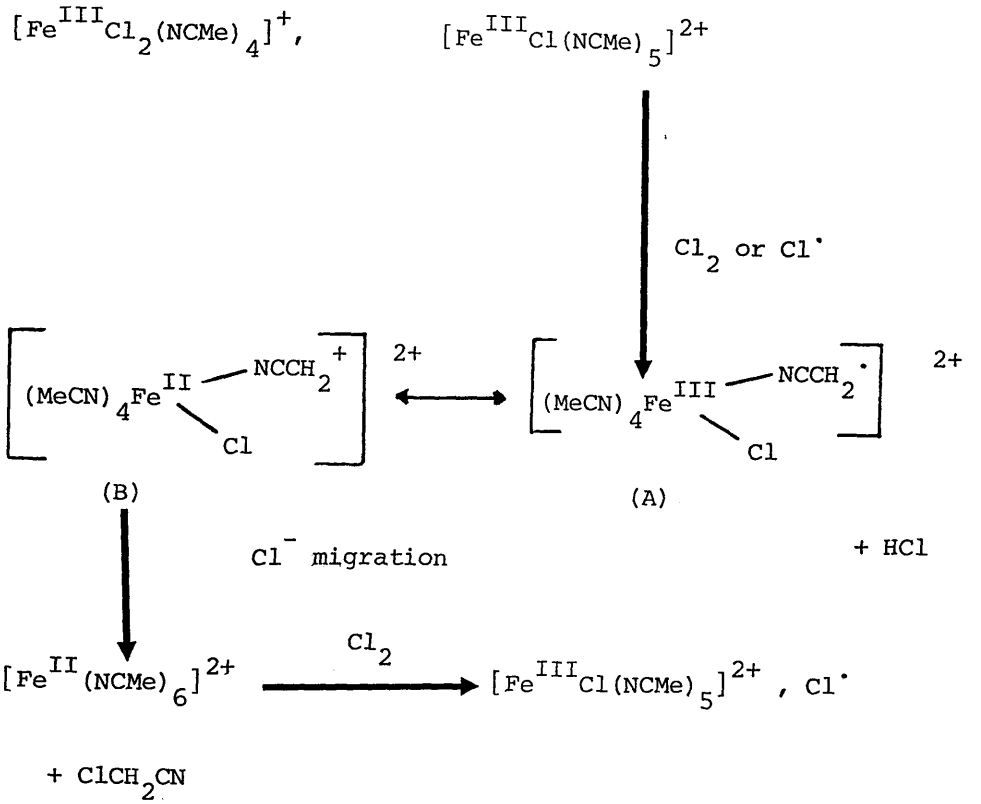

$UF_{5-x}Cl_x$ tppo, $x \geqslant 3$
0·5
Absorbance
600
800
1000
1200
1400
1600
λ n m

Figure 4.7

chloridefluorides. Trimethylchlorosilane and solid UF_5 do not react in the presence of CH_2Cl_2 over 24h and there is no reaction between solid UF_5 and UCl_5 dissolved in CCl_4. The use of a donor solvent such as acetonitrile to dissolve the UF_5 seems to be important. The lability of the U^{V}-F and U^{VI}-F bonds in UF_6, βUF_5 or the $[UF_6]^-$ anion with respect to substitution has been confirmed by ^{18}F radiotracer studies under heterogenous conditions and in MeCN solution.[109] Halogen exchange also occurs to give uranium(V) chloridefluorides when UF_5 reacts with BCl_3 or $B[OCCl(CF_3)_2]_3$ in MeCN.[109]

The initial step in the reaction of Cl_2 and UF_6 in MeCN is very fast and involves a redox reaction, where the U^{VI} is reduced to a U^{V} species. Reduction of high oxidation state chlorides by MeCN is well known[110] and in some cases evidence for the formation of chlorinated organic products has been obtained.[111] It has been shown that when $FeCl_3$ is used as a catalyst for chlorination by Cl_2, consideration should be given to the conditions necessary for an efficient Fe^{III}-Fe^{II} redox cycle.[112] Under the conditions investigated, the yield of chlorinated material, chloroacetonitrile, after 20h was significant only when both $FeCl_3$ and Cl_2 were present in MeCN solution. Trichloroacetonitrile was also formed when a longer reaction time was used or if hexakis(acetonitrile)iron(II) hexafluorophosphate was present. The reaction pathway proposed is shown in Figure 4.5.

Figure 4,5



Involvement of the intermediate (B) is required to produce Fe^{II} and this pathway could account for the accelerated reduction of Fe^{III} in the presence of Cl_2. In the present work there is evidence for chlorinated organic products, and the reduction of UF_6 in MeCN is increased significantly by the addition of Cl_2. Although no conclusive evidence can be presented for the reaction, the redox chlorination of solvent explanation seems a plausible hypothesis.

Molecular chlorine has been shown to chlorinate MeCN very slowly ca 20h at room temperature to give monochloroacetonitrile, no trichloroacetonitrile was observed.[99] It was assumed that HCl was released but this was not detected due to consumption in the redox reactions involved. As chlorination of MeCN occurs in the $MeCN/Cl_2$ system, it suggests a free radical mechanism is

involved. It has been observed that treatment of MeCN by HCl increases the rate of chlorination.[113] If the first step in the chlorination is the attack of the MeCN by a free radical $Cl^{\cdot}$, leading to the formation of CH_2ClCN then HCl will be liberated. The HCl liberated adds to the partly chlorinated nitrile forming a nitrilium salt which is more readily chlorinated than MeCN[113] Scheme 4.1

$$Cl^{\cdot} + CH_3CN \longrightarrow {}^{\cdot}CH_2CN + HCl$$

$${}^{\cdot}CH_2CN + Cl_2 \longrightarrow CH_2ClCN + Cl^{\cdot}$$

$$CH_2ClCN + HCl \xrightarrow{\text{slow}} (CH_2ClCNH)^+ (Cl)^-$$

$$[CH_2ClCNH]^+Cl^- + Cl_2 \xrightarrow{\text{rapid}} [CHCl_2CNH]^+ [Cl]^- + HCl$$

$$[CHCl_2CNH]^+Cl^- + Cl_2 \xrightarrow{\text{rapid}} [CCl_3CNH]^+[Cl]^- + HCl$$

$$[CCl_3CNH]^+Cl^- \longrightarrow CCl_3CN + HCl$$

The presence of Cl^- could rapidly exchange with the $UF_5(NCMe)_x$ present giving the halogen exchange products.

Anhydrous hydrogen chloride can react with MeCN to form an acetohalogen imidium-halide complex[114] according to the equation.

$$2HCl + MeCN \longrightarrow \left[CH_3-\underset{Cl}{\overset{|}{C}}=N\begin{matrix}H\\H\end{matrix} \right] + [Cl]^-$$

The structure of the above complex was determined by single crystal neutron diffraction. The complex was made during the course of the present work, but when dissolved in MeCN at room temperature it dissociated to give HCl and MeCN.

Wolf et al [115] found that when UF_6 and liquid Br_2 were allowed to stand overnight, a small amount of white material formed. This was identified as β-UF_5. It was found that HBr present in the Br_2 as an impurity caused the formation of β-UF_5. From this discovery a preparation for greater yields of product was derived, the authors reacted gas phase HBr and UF_6 at 338 K to yield β-UF_5.

It is possible that if some HCl is formed initially in the chlorine reactions, it could react with UF_6 to give UF_5, HF and $\frac{1}{2}Cl_2$ analogous to the HBr, UF_6 preparation of β-UF_5.

The presence of hydrogen halides in reaction mixtures, could be a reason for the difficulty in obtaining a single product from the reactions. When volatile material was removed from a reaction mixture of Cl_2, UF_6 and MeCN after 1h reaction, HCl was detected in the gas phase by infrared spectroscopy. The product obtained from this preparation was green and homogeneous. Its $^{13}C\{H\}$ nmr spectrum is tabulated (Table 4.8). By removing the volatile hydrogen halides after one hours reaction a better product was obtained which may have been due to lack of solvent attack by HF or HCl. From all the spectroscopic evidence and because of the range of products obtained from the reactions, it is likely that a mixture of species is present at any one time.

The presence of HF cannot be excluded from the analysis, because etching occurs on the surface of the reaction vessels and there are bands consistent with the presence of SiF_4 in some infra red spectra. The presence of SiF_4 is characteristic of HF attacking the Pyrex glass of the vessels.

EXPERIMENTAL

Unless described below, procedures for purification of reagents, manipulation of products and spectroscopic measurements were as described in Chapter 7.

Molecular chlorine (Matheson Ltd) was degassed and allowed to stand over $KMnO_4$ at 233 K for several hours, it was then distilled at 203 K onto fresh P_2O_5. The P_2O_5 distillation step was repeated and the Cl_2 was stored over P_2O_5 at 77 K until required.

Hydrogen chloride gas was generated in Pyrex apparatus consisting of a reaction vessel with a pressure equilibrating dropping funnel attached, to which a series of traps were connected, Figure 4.6. Trap (I) contained P_2O_5 and was cooled to 213 K using a dichloromethane/CO_2 slush bath. Trap (II) contained P_2O_5 and was cooled to 183 K in a methanol/liquid nitrogen bath. The collection vessel (III) was fitted with P.T.F.E/Pyrex vacuum stop-cocks (J. Young) enabling it to be isolated from the rest of the apparatus. Ten millilitres of 35.4% aqueous hydrochloric acid (Hays Chemicals) were added dropwise to concentrated sulphuric acid. The HCl gas generated was distilled through traps (I) and (II) and collected in trap (III) at 153 K. Trap (III) was transferred to a vacuum line where the HCl was degassed, vacuum distilled twice from 186 K to 153 K onto P_2O_5 and stored over P_2O_5 in a Pyrex vessel at 77 K.

Apparatus for the preparation of Hydrogen Chloride.

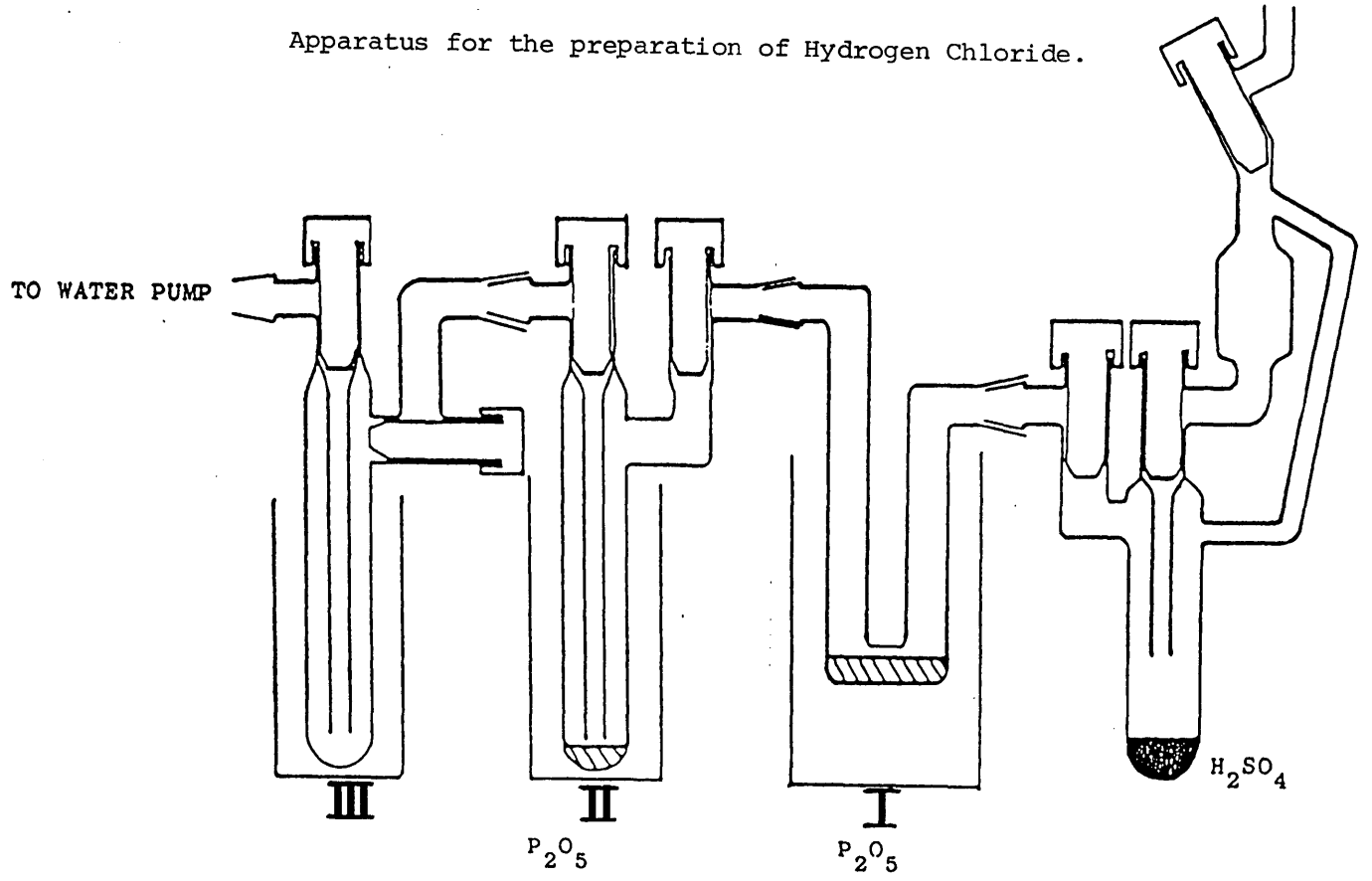


Figure 4.6

Reaction of Molecular Chlorine with Uranium Hexafluoride in Acetonitrile.

A solution of Cl_2 (2.0 mmol) in MeCN (5 cm^3) was prepared *in vacuo* and UF_6 (*ca* 0.5 mmol) added to the frozen solution by vacuum distillation into a double limb vessel. On warming the mixture to room temperature a lime green solution formed. Removal of the volatile material left a pale green solid whose composition, appearance and spectroscopic properties varied. These are described in more detail in Tables 4.3 to 4.9.

Reaction of Molecular Chlorine with Uranium Hexafluoride in Acetonitrile followed by Electronic Spectroscopy.

A solution of Cl_2 (2 mmol) in MeCN (5 cm^3) was prepared in a Spectrosil cell U.V. vessel, UF_6 (0.5 mmol) was added and the solution warmed to room temperature. The electronic spectrum of the solution was recorded immediately, then at varying intervals up to 72h. The electronic spectra are shown in Figure 4.2 and the species present are shown in the flow diagram (4.1). By comparison with the literature the initial species formed was $UF_5(NCMe)_x$, followed by $UF_3Cl_2(NCMe)_x$ after 3.5h reaction, finally $UFCl_4(NCMe)_x$ was formed after *ca* 15h reaction time.

Reaction of Hydrogen Chloride with Uranium Hexafluoride in MeCN.

Hydrogen chloride gas (0.6 mmol) was distilled onto a mixture of frozen UF_6 (0.1 mmol) in MeCN (5 cm^3) at 77 K and allowed to warm to room temperature. A green solution formed and its electronic spectrum which is shown in Figure 4.3 resembled that of $UFCl_4(NCMe)_x$.[108]

Reaction of Hydrogen Chloride with Uranium Hexafluoride in Acetonitrile with Subsequent Addition of Triphenylphosphine Oxide.

Triphenylphosphine oxide (0.5 g) was added to a frangible ampoule and placed in a double limb vessel. Acetonitrile (5 cm^3) and UF_6 (0.085 mmol) were distilled in by low temperature distillation. Hydrogen chloride (ca 0.5 mmol) was added and the mixture allowed to warm from 77 K to room temperature, the vessel was shaken and the solution left for one hour. The ampoule was broken allowing the tppo to mix with the solution. Removal of volatile material left a green crystalline solid. The solid was identified by its infra red and electronic spectra as predominantly UF_5.tppo, by comparison with the literature values.[108] The i.r. spectrum is tabulated in Table 4.10 and the electronic spectrum is shown in Figure 4.4. This experiment was repeated but tppo was added after several hours reaction. A sticky yellow solid was obtained after removing the volatile material. After pumping for several hours the product remained sticky. Holloway et al[108] reported that the more chlorinated the product the more yellow the colour of the product and it took longer to remove the last traces of solvent. The quality of spectra from this sample was not very good due to the sticky nature of the product, but it appeared to be a $UF_{5-x}Cl_x$.tppo species where x is ≥ 3.

CHAPTER 5

OXIDATION OF TELLURIUM IN ACETONITRILE.

INTRODUCTION

After investigating the properties of the compounds formed between the group VII elements iodine, bromine and chlorine with various oxidising agents in acetonitrile, an example of a group VI element was investigated; tellurium was chosen. This gave an example of oxidation under heterogeneous conditions. The halogens are all soluble in MeCN; tellurium being insoluble, may react differently, for example due to some surface effect and hence the reactions are more likely to resemble those of metals. The group VII elements are non metals where as tellurium shows some metallic character, conducting electricity for example. Its specific resistivity = 2×10^5 $\mu\ \Omega$-cm at 25^oC [125], but it has a negative temperature coefficient of resistivity which is usually considered to be a characteristic of non metals. If tellurium behaved like a metal a solvated cation $Te(NCMe)_x^{n+}$ could be expected, but if it behaved like a non metal a species such as $Mo^{VI}TeF_4$ could be formed analogous to $MoOF_4$.

RESULTS

Oxidation of Tellurium by Uranium Hexafluoride in Acetonitrile.

When UF_6 was distilled into a vessel containing Te and MeCN, a light green colour was observed when the reaction mixture reached room temperature. The colour darkened to a greenish-blue as the mixture was shaken for 30 minutes. Removal of the volatile material resulted in the precipitation of a green crystalline solid as the solution became more concentrated. If the solvent was removed too quickly the crystallinity was lost and a powdery material was obtained. The solid had the empirical formula $C_{10}H_{15}F_{24}N_5TeU_4$ from a full elemental analysis. The course of the reaction was followed by electronic spectroscopy at room temperature, groups of bands due to the anion $[UF_6]^-$ and to the species $UF_5(NCMe)_x$ were observed. The bands increased in intensity with time. The greenish-blue solid isolated could be redissolved in MeCN to give an electronic spectrum identical to that obtained from the reaction mixture. The solid was stable to hydrolysis at 273 K if stored in vacuo and could be kept for several months in a freezer. When an attempt was made to investigate the crystals by X-ray crystallography, the solid decomposed within 48 hours in the X-ray capillaries. This was probably due to hydrolysis occurring as the solid was manipulated in the dry box or to hydrolysis occurring in the fine quartz capillaries used for X-ray analysis. These are difficult to degass properly.

The vibrational spectra of the solid was consistent with the presence of coordinated MeCN, octahedral $[UF_6]^-$ and UF_5.NCMe. Band assignments (Table 5.1) were made by comparison with the

Table 5.1 Vibrational Spectra of the Product from the Reaction of Tellurium and Uranium Hexafluoride in Acetonitrile.

$[TeF_3(NCMe)_2][UF_6]3UF_5NCMe$

Infrared ν_{max} cm^{-1}	Raman $\Delta\nu$ cm^{-1} Solid	Solution	Assignments
2312 s			CH_3 def + CC str
2284 s			CN str
1040 m			CH_3 rock
970 m			C-C str
940 m			C-C str
723 m			
680 m			
	612	612*	ν_1 $[UF_6]^-$
	592	604*	U-F str
570 s			δ(Te-F) ?
520vs			ν_3 $[UF_6]^-$
390 m			CCN def
315 w	308		δ(Te-F) ?
265 w	243		δ(Te-F) ?

* both polarisable in MeCN.

s = strong; m = medium; w = weak;

def = deformation mode

str = stretching mode

vibrational spectra of the Thallium(III) hexafluorouranate(V) salt[35], salts of metal cations containing coordinated MeCN[97], BF_3NCMe[116], SbF_5NCMe[117] and the adduct UF_5NCMe.[100] The Raman spectrum of the solid contained bands at 612 and 592 cm^{-1}; the band at 612 cm^{-1} could be assigned to $\nu_1[UF_6]^-$ by comparison with $[Tl(MeCN)_5][UF_6]_3$[35], and the band at 592 cm^{-1} to a U-F vibration arising from UF_5NCMe.[103] The vibrational spectra of the $[Tl(MeCN)_5][UF_6]_3$ salt and the adduct UF_5.NCMe are listed in Tables 5.2 and 5.3 for comparison. The band at 570 cm^{-1} in the infrared spectrum of the solid can be tentatively assigned to a Te-F stretching vibration. These are known to occur in this region, for example $pyTeF_4$[124] has two bands at 570 and 555 cm^{-1} assigned to ν(Te-F). Berry et al[100] found that in MeCN solution UF_5NCMe contained two bands at 611 and 602 cm^{-1} which were completely polarised. A MeCN solution of the solid $C_{10}H_{15}F_{24}N_5TeU_4$ contained Raman bands at 612 and 604 cm^{-1} which were both polarised. From this evidence it appears that UF_5NCMe is present in the solid material. The two bands at 308 and 243 are tentatively assigned to Te-F vibrations by comparison with the Raman spectrum of TeF_4[128] which has two bands at 314 and 230 cm^{-1}; these bands were unassigned. This leaves two bands unassigned in the vibrational spectrum of the solid. These occur at 723 and 680 cm^{-1}, the band at 723 cm^{-1} is assigned to Nujol by comparison with a genuine Nujol spectrum.

The electronic spectrum of the solid in MeCN contained bands attributable to a mixture of $[UF_6]^-$ and UF_5NCMe, (Figure 5.1). The electronic spectrum of UF_5 in MeCN consists of four groups of bands and is similar to that of $[UF_6]^-$, but there are sufficient differences in band position and in the associated vibronic structure

Table 5.2 UF_5NCMe Assignments (Literature)

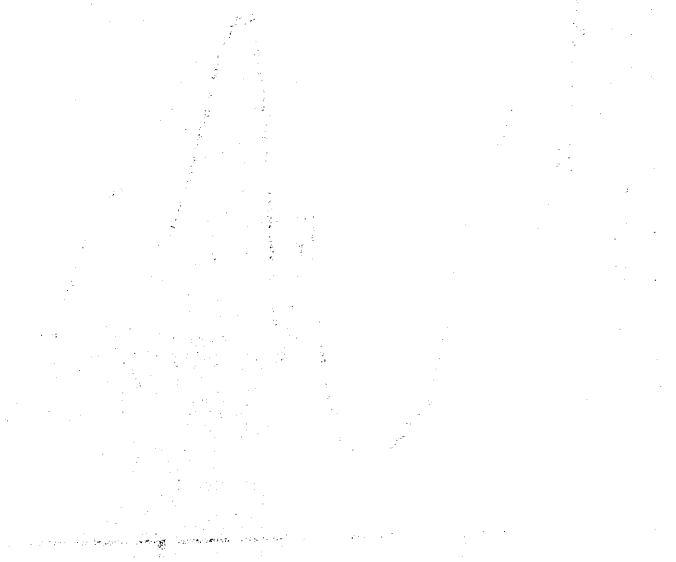
Infrared[108] ν_{max} cm^{-1}	Infrared[103] ν_{max} cm^{-1}	Assignments
2322 s	2330 vs	CH_3 def + C-C str
2284 s	2302 vs	CN str
	1114 w	
1030 s	1034 s	CH_3 rock
968 s	967 vs	C-C str
612 w, sh	730 m	
582 vs	597 vs	
	580 vs	
551 w) 522 s)		U-F str
436 w		
386 w	384 m	C-CN bend
	(593 cm^{-1} Raman)	ν U-F

*Berry et al[100] found two polarised Raman bands in MeCN solution at 611 and 602 cm^{-1}, assigned to νU-F vibrations. Two bands at 530 and 350 cm^{-1} were also assigned to νU-F vibrations from their I.R. data.

Table 5.3 Vibrational Spectrum of $[Tl(MeCN)_5][UF_6]_3$ [35]

Infrared ν_{max} cm^{-1}	Raman $\Delta\nu$ cm^{-1}	Assignment
2320 s		CH_3 def + C-C str
2295 s		CN str
945 s		C-C str
725 m		U-O
	613*	ν_1 $[UF_6]^-$
520 vs vbr		ν_3 $[UF_6]^-$
	194	ν_5 $[UF_6]^-$
145		ν_4 $[UF_6]^-$

*Polarised in MeCN solution.



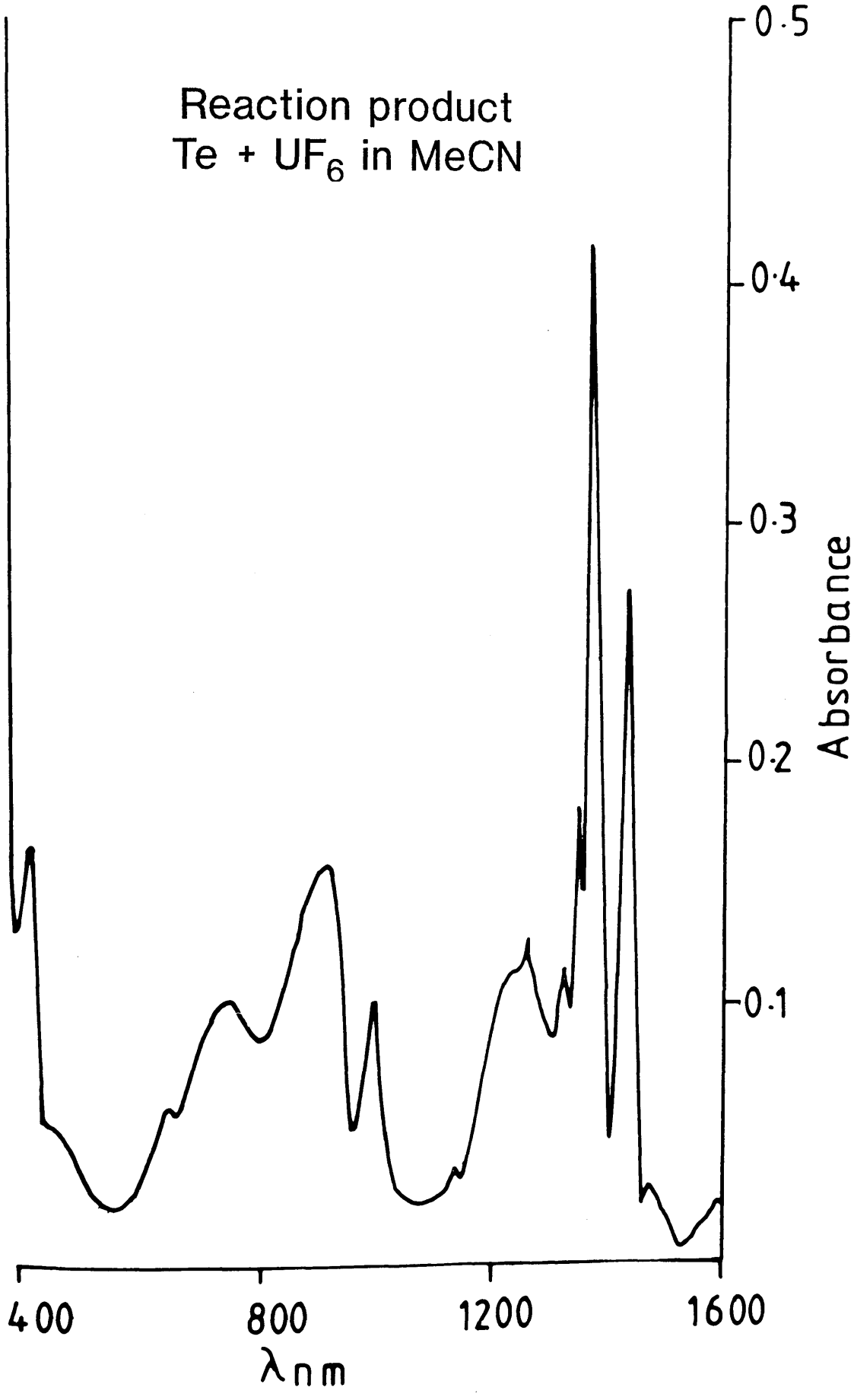

Reaction product
Te + UF_6 in MeCN
0·5
0·4
0·3
0·2
0·1
Absorbance
400
800
1200
1600
λnm

Figure 5.1

to enable the two species to be distinguished. When the two species are mixed, the spectrum is complicated but the different intensities of the bands enable the two species to be identified. Electronic spectra due to the $[UF_6]^-$ anion and UF_5.NCMe are shown in Figure 5.2. The bands were assigned by comparison with $[Tl(MeCN)_5][UF_6]_3$ in MeCN,[35] $[AsPh_4][UF_6]$ [84] in MeCN and UF_5NCMe in MeCN.[100] The UF_5.NCMe bands dominate the electronic spectrum of the reaction product, this is because the $[UF_6]^-$ spectrum is obscured beneath the bands due to UF_5NCMe, which has more broad bands than does $[UF_6]^-$ the spectra of which is sharper and more intense.

The ^{125}Te n.m.r spectrum of the reaction product in CD_3CN/EtCN contained a broad singlet at 1313 p.p.m, with respect to Me_2Te. This is assigned to the TeF_3^+ cation by comparison with known Te compounds (Table 5.4).

The spectroscopic data enable conclusions to be drawn about the nature of the product and these will be discussed later in the chapter.

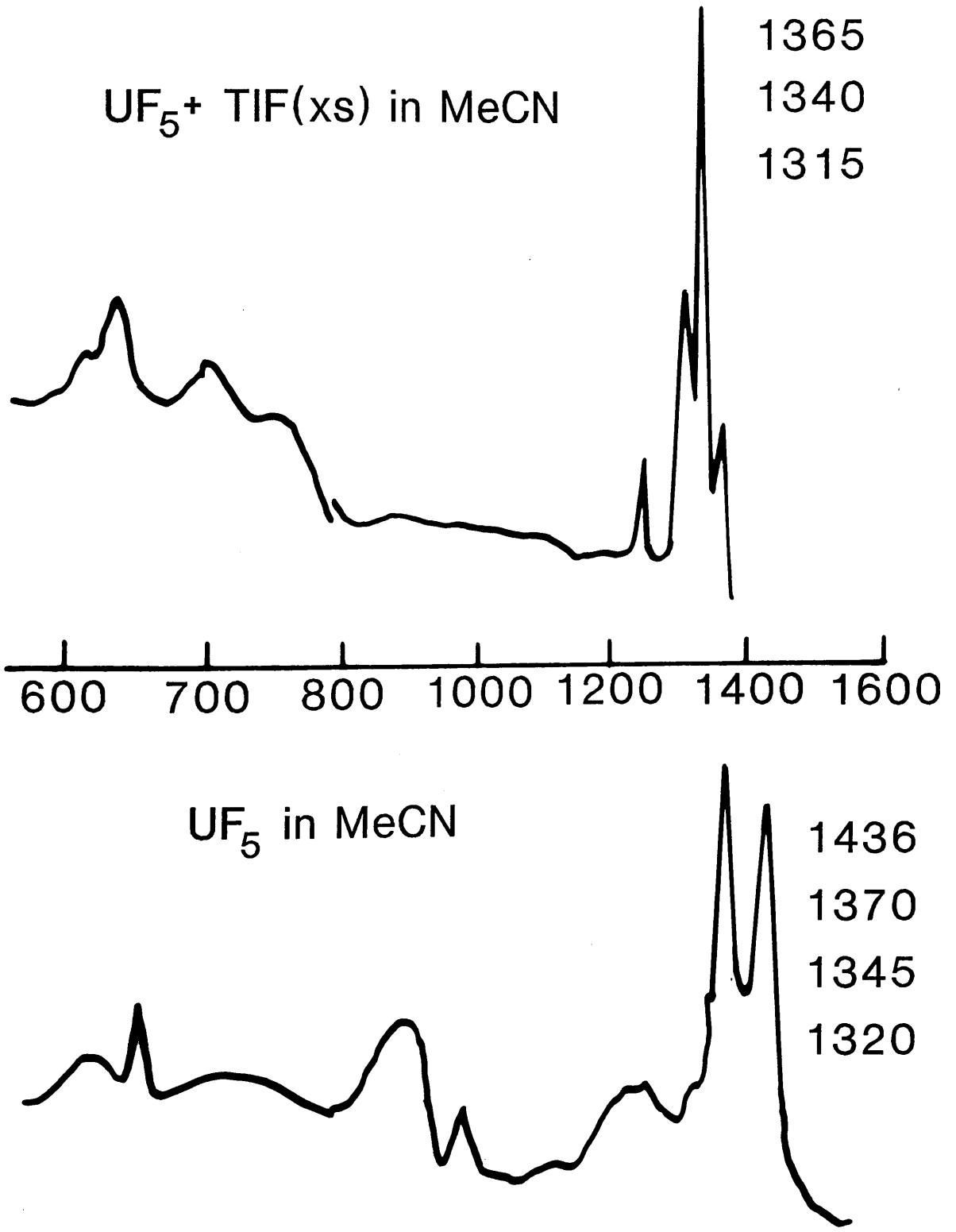

UF5+ TIF(xs) in MeCN
1365
1340
1315
600
700
800
1000
1200
1400
1600
UF5 in MeCN
1436
1370
1345
1320

Figure 5.2

Table 5.4

COMPOUND	δ ^{125}Te ppm	Temperature (K)	Solvent	Reference
$[TeF_3(NCMe)_2][MoF_6]3MoF_5NCMe$	1369	293→213	CD_3CN/EtCN	This work
$[TeF_3(NCMe)_2][UF_6]3UF_5NCMe$	1313	293→213	CD_3CN/EtCN	This work
$[TeF_3(NCMe)_2][MoF_6]3MoF_5NCMe$	1325	200	SO_2	This work
TeF_3^+	1382	200	SO_2	This work
TeF_3^+	1382	200	SO_2	[126]
TeF_4	1317	200	SO_2	[126]
Te_6^{4+}	152		H_2SO_4/SO_3	[127]
Te_4^{2+}	2811		H_2SO_4/SO_3	[127]

All chemical shifts are referred to Me_2Te; low field shifts are positive.

Oxidation of Tellurium by Molybdenum Hexafluoride in Acetonitrile.

When tellurium and molybdenum hexafluoride were allowed to react in acetonitrile, mole ratio Te:MoF_6 1:6, that is one mole of Te to approximately six of the hexafluoride, a pink colour was observed at the Te surface as the solution warmed to room temperature. After shaking, the colour became more intense. After ca. 1 hour the solution was blood-red. Removal of the volatile material left an off-white product. This material was obtained in a crystalline condition if the volatile material was removed slowly over the space of three to four hours. The pale yellow solid had the empirical formula $C_{10}H_{15}F_{24}N_5TeMo_4$ from a full analysis. The reaction was followed by electronic spectroscopy at room temperature. A band λ_{max} = 445 nm was observed initially, and increased in intensity with time. The spectrum also had a large absorbance near 300 nm which was too intense to be measured at the concentrations used. When the solid material was isolated and redissolved in MeCN, a pale yellow solution was obtained with λ_{max} = 320, 242 and 205 nm. This spectrum is shown in Figure 5.3.

Electronic spectra of tellurium cationic species have been recorded in acidic media.[27] It was found that when Te was dissolved in a strongly acidic solvent, for example oleum, a red species was obtained, λ_{max} = 512 nm for 15% oleum. As the strength of the oleum was increased, the band position moved to higher energy, λ_{max} = 475 nm for 30% oleum. The species responsible for these bands is the cation Te_4^{2+}. By comparison with this work the band initially observed in MeCN at λ_{max} 445 nm was assigned to Te_4^{2+}. The implications of this will be dealt

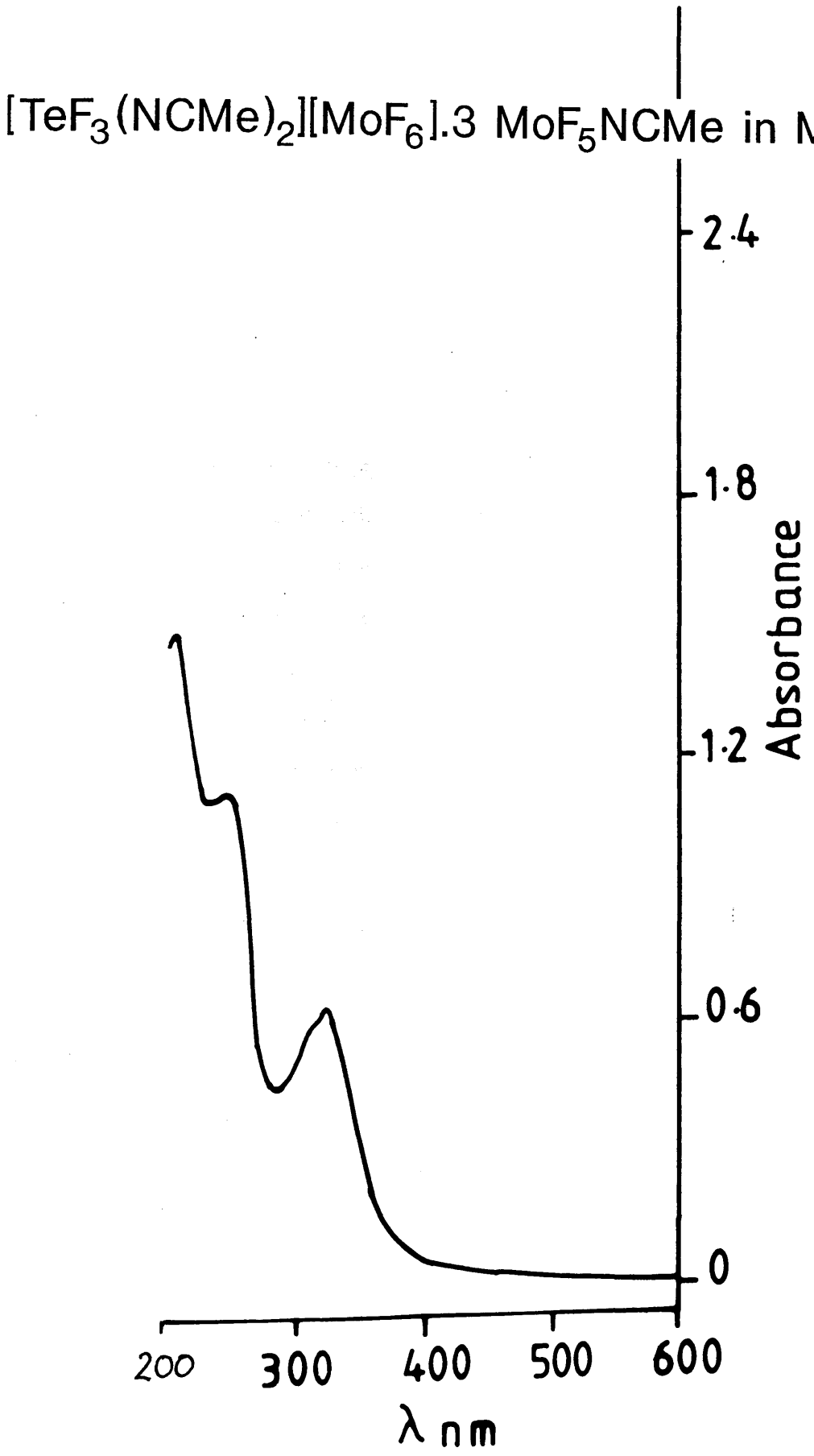

[TeF3(NCMe)2][MoF6].3 MoF5NCMe in MeCN
2·4
1·8
1·2
0·6
0
Absorbance
200
300
400
500
600
λ nm

Figure 5.3

with later in the chapter.

The vibrational spectra of the solid consisted of bands which could be assigned by comparison with salts of metal cations containing coordinated MeCN[97], the hexafluoromolybdate(V) anion[96], MoF_5NCMe [118], and $[I(NCMe)_2][MoF_6]$.[39] The vibrational spectra are tabulated in two tables; Table 5.5 contains the bands assigned to the coordinated acetonitrile and Table 5.6 contains the bands assigned to M-F vibrations (where M = Te or Mo). Spectra of a known $[MoF_6]^-$ salt and MoF_5.NCMe are tabulated in Table 5.7 to enable comparisons to be made. All the bands observed from the solid material can be accounted for by comparison with the spectra of the anion $[MoF_6]^-$, coordinated MeCN and the adduct MoF_5.NCMe. The Raman spectra of the reaction product and of the solid dissolved in MeCN solution consisted of two bands at 705 and 683 cm^{-1}. These were both completely polarised in MeCN solution. The bands were assigned to $\nu_1[MoF_6]^-$ and ν_1 MoF_5.NCMe. The intensity of the band at 705 cm^{-1} in the solution spectrum was about four times as intense as that of the 683 cm^{-1} band. In this region Te-F vibrations may be expected, and they could possibly contribute to the band intensities. The Raman spectrum is shown in Figure 5.6.

The ^{125}Te n.m.r spectrum of the reaction product gave a broad single resonance at 1369 p.p.m with reference to Me_2Te. This was assigned to TeF_3^+ by comparison with known Te compounds which are listed in Table 5.4. In an attempt to narrow the signal, the adduct AsF_5.NCMe was added to the n.m.r solution. The adduct AsF_5NCMe would be expected to react with any free F^- forming the stable anionic species $[AsF_6]^-$. The width of the ^{125}Te signal decreased very slightly, but the decrease was not

Table 5.5 Vibrational Spectrum of the product from the reaction of Tellurium and Molybdenum Hexafluoride in Acetonitrile.

$[TeF_3(NCMe)_2][MoF_6]$ $3MoF_5.NCMe$

Bands due to coordinated acetonitrile

Infrared ν_{max} cm^{-1}	Assignments
3270 m	comb.
3240 m	comb.
3015 m	asym C-H str
2944 m	sym C-H str
2328 s 2320 s	CH_3 def + C-C str
2295 s	CN str
1410 m	CH_3 def
1365 m	CH_3 def
1030 s	CH_3 rock
954 s	C-C str
418 m	CCN def

def = deformation mode str = stretching mode

asym = asymmetric sym = symmetric

comb = combination band.

Table 5.6 Vibrational Spectra of the product from the reaction of Tellurium with Molybdenum Hexafluoride in Acetonitrile. $[TeF_3(NCMe)_2][MoF_6]$ $3MoF_5NCMe$

M-F Region where M = Mo or Te

Infrared ν_{max} cm^{-1}	Raman $\Delta\nu$ cm^{-1}	Assignments
722 m		comb.
	705* (8)	ν_1 MoF_5
703 s		Mo-N
	683* (2)	ν_1 $[MoF_6]^-$
650 s		Mo-F axial
635 vs		ν_3 $[MoF_6]^-$
295 s		F-MoF_4 def
240 s		MoF_4 in plane def
225 s		Te-F
	220	ν_5 $[MoF_6]^-$
	215	Te-F

*Both completely polarised in MeCN solution.

Raman intensities in brackets.

Table 5.7 Vibrational Spectra of the anion $[MoF_6]^-$ and the adduct MoF_5NCMe.

$[MoF_6]^-$ — J. Shamir et al [96]

Infrared ν_{max} cm^{-1}	Raman $\Delta\nu$ cm^{-1}
	688 ν_1
635 ν_3	
	450 ν_2
232 ν_4	
	236 ν_5

MoF_5NCMe — J.C. Fuggle et al [118]

Infrared ν_{max} cm^{-1}	Raman $\Delta\nu$ cm^{-1}
705 m	
	697
650 vs	
	665
635 sh	

Raman Spectrum of $[TeF_3(NCMe)_2][MoF_6].3MoF_5NCMe$

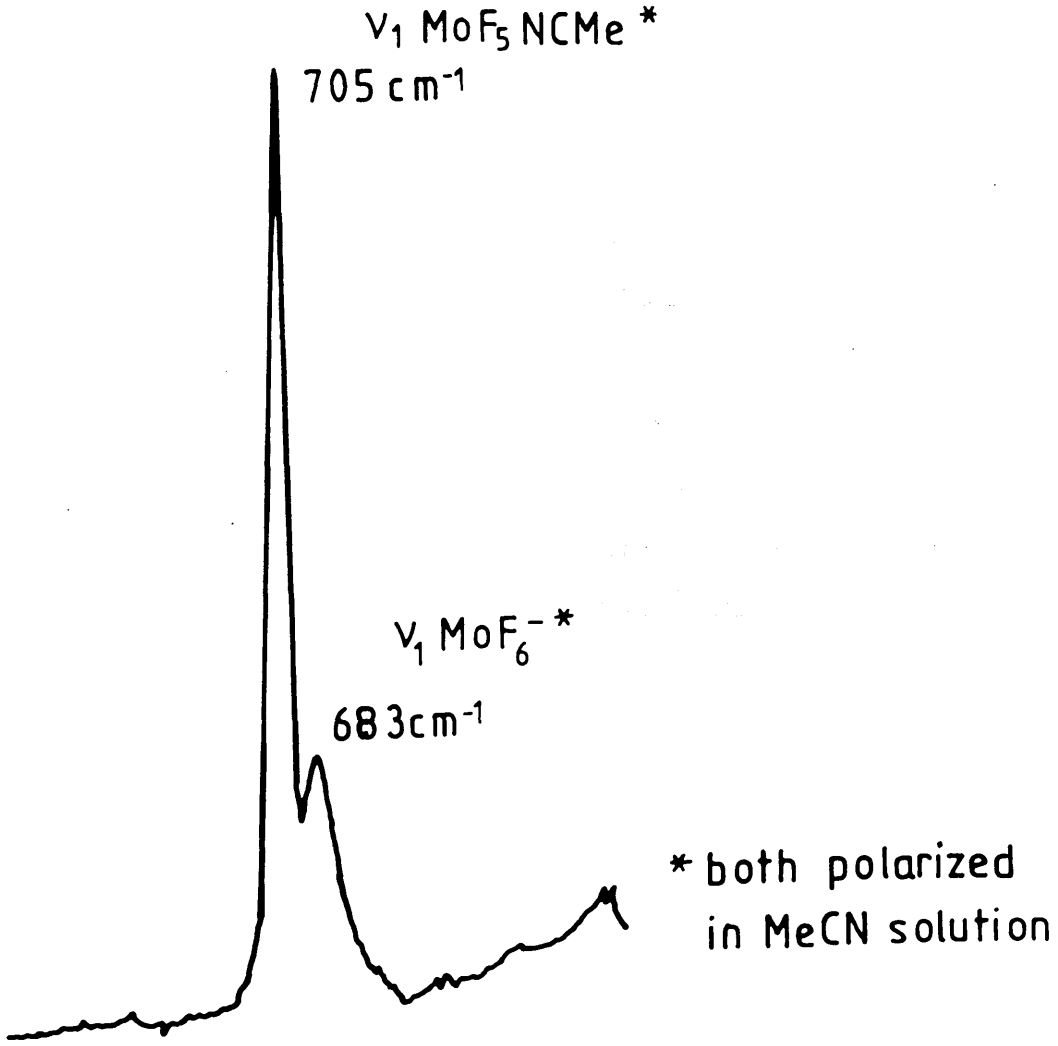


Figure 5.6

very significant,

Oxidation of Tellurium by Nitrosonium Hexafluorophosphate in Acetonitrile.

A solution of $NOPF_6$ in MeCN was added to Te, mole ratio $Te:NOPF_6$ = 1:3; that is a ratio of one mole of Te to three of $NOPF_6$; bubbles of gas were released immediately at the Te surface; a pink red colour was observed "bleeding" from the Te. The solution changed from pink to orange after ca 2 hours. Removal of the volatile material, after first degassing the solution to remove the non condensable gas presumed to be NO, left a sticky brown viscous oil. A detailed spectroscopic examination could not be undertaken because of the nature of the product. The course of the reaction was followed by electronic spectroscopy, a band was observed λ_{max} = 522 nm after 10 minutes reaction. The band position shifted to higher energy with time λ_{max} 445 nm after 5 hours. The species assigned to the band was Te_4^{2+} by comparison with Te in acidic media.[27]

Oxidation of Tellurium by the Acetonitrile adducts of Antimony Pentafluoride and Arsenic Pentafluoride in Acetonitrile.

A solution of MF_5.NCMe (M = As or Sb) in MeCN was added to Te, no immediate change was observed. When the solutions were shaken overnight a pale pink colour was observed. This gradually darkened over a period of 5 days. Removal of the volatile material left pale pink products mixed with some colourless material. The vibrational spectra of the solids

contained bands due to the starting materials and bands due to the anions $[SbF_6]^-$ or $[AsF_6]^-$. The spectra were assigned by comparison with $LiSbF_6$, $CsAsF_6$[98] and by comparing their spectra with that of the adducts AsF_5NCMe and SbF_5NCMe. The electronic spectra of the solids in acetonitrile contained bands at λ_{max} = 523 nm, assigned to Te_4^{2+} by comparison with the literature.[27]

Reaction of Tellurium with Tungsten Hexafluoride in Acetonitrile.

When tellurium and tungsten hexafluoride were added to MeCN mole ratio $Te:WF_6$ 1:6, that is a ratio of one mole Te to approximately six of tungsten hexafluoride, and shaken for two weeks, no colour change was observed. Removal of the volatile material left unreacted Te. From this it was assumed no reaction had occurred and no further investigation was carried out.

DISCUSSION

Evidence for the Formulation of Products as $[TeF_3(NCMe)_2]$-$[MF_6]$ $3MF_5NCMe$ M = Mo or U.

As discussed in earlier chapters, two types of cation have been formed from the oxidation of I_2 or Br_2 using MeCN as solvent, the $[I(NCMe)_2]^+$ cation and the $[Me\overbrace{C=N-(Me)C=N-(Me)C=N}Br]^+$ cation. By extending the work to include tellurium a third type of cation was obtained. The products from the oxidations involving the stronger oxidising agents. UF_6 or MoF_6 are crystalline solids which are formulated on the basis of their analyses, ^{125}Te n.m.r, vibrational and electronic spectroscopies as $[TeF_3(NCMe)_2][MF_6].3MF_5$-NCMe (M = Mo or U). The vibrational spectra of the compounds contain two polarised bands in MeCN solution, these could not both arise from the $[MF_6]^-$ anions. The M-F regions of the infrared spectra were more complex than expected for simple $[MF_6]^-$ anions. Individual assignments were complicated by the broadness of the bands in this region and the close proximity of different M-F containing species having bands of similar energies. From the analytical results, a possible structure for the compounds is a Te^{IV} species with five coordinated MeCN ligands, with the lone pair on the Te completing a pseudo-octahedral arrangement. This i.e. $[Te(NCMe)_5]^{4+}$ would be counterbalanced by four $[MF_6]^-$ anions giving the formulation $[Te(MeCN)_5][MF_6]_4$. This species does not however account for all the spectroscopic data obtained. By considering other tellurium cations that have been reported in the literature, it is apparent that the TeF_3^+ cation is a possibility. Greenwood et al[124] prepared Tellurium(IV) Fluoride adducts with organic ligands. The adducts have the stoichiometry $LTeF_4$ and are formulated as

$[L_2TeF_3^+][TeF_5^-]$ from their vibrational spectra, where L = pyridine, trimethylamine or dioxan. The crystal structure of the $TeF_4.2SbF_5$ adduct is known[119] and is $TeF_3^+Sb_2F_{11}^-$ formed according to the equation

$$TeF_4 + 2SbF_5 \longrightarrow TeF_3^+ Sb_2F_{11}^- \qquad (1)$$

The cation has C_{3v} symmetry with a mean Te-F distance of 1.84 Å, and three long contacts of 2.54, 2.55 and 2.69 Å to bridging fluorine atoms, this gives a much distorted octahedral coordination for Te, very similar to $[SeF_3]^+[Nb_2F_{11}]^-$.[120] Collins et al[126] when studying the donor properties of $Te(OTeF_5)_4$ by ^{125}Te n.m.r spectroscopy, prepared the TeF_3^+ cation in SO_2 by a reaction between TeF_4 and AsF_5 according to the equation

$$TeF_4 + AsF_5 \xrightarrow{SO_2} TeF_3^+ AsF_6^- \qquad (2)$$

The ^{125}Te n.m.r spectrum of the TeF_3^+ cation consists of a singlet at 1383 p.p.m. referenced to Me_2Te which is split into a quartet at 200 K, the Te-F coupling constant being 2905 Hz. Excess AsF_5 was used in solution to reduce line broadening by suppression of fluoride exchange. This preparation was repeated for comparison purposes in the present work and the TeF_3^+ spectrum is shown in Figure 5.4. The new compounds made in this work were studied by ^{125}Te n.m.r spectroscopy. The signals obtained were very broad, and cooling to 200 K in SO_2 still produced a broad resonance although a little line narrowing occurred; the quartet of signals expected for TeF_3^+ could not be obtained. The resonances obtained were in the region expected for a TeIV species shown in Table 5.4. The M-F bonds in the MF_6^- anions are known

^{125}Te nmr of the TeF_3^+ cation

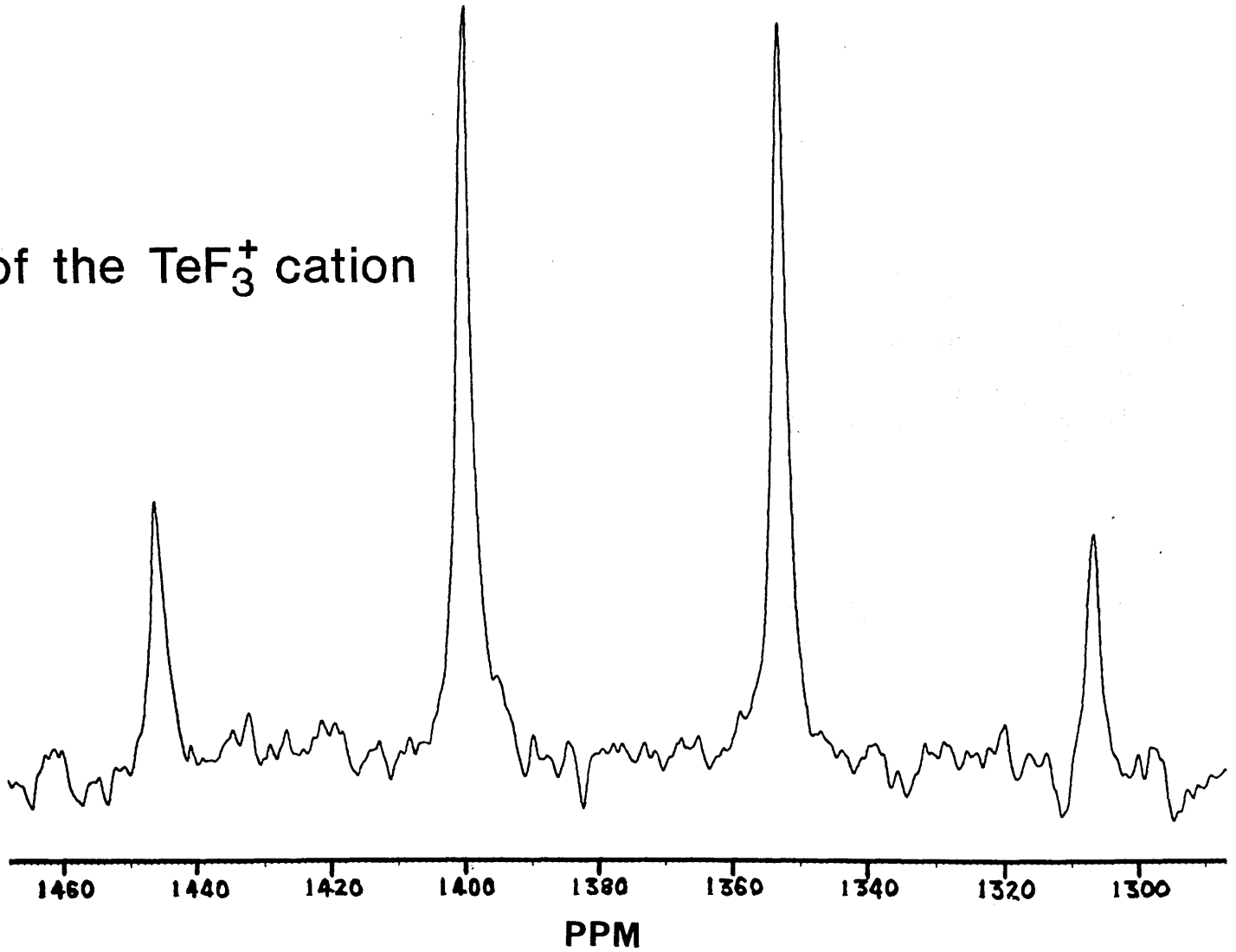


Figure 5.4

to be labile[109] and could provide a mechanism for F^- transfer between M^V and Te^{IV}. Similarly exchange between TeF_3^+ and $[MF_6]^-$ or MF_5NCMe could be expected. Thermodynamically Te^{4+} would be very polarising, and could be expected to pull F^- from a species to reach a more stable state, whilst kinetically the lability of F^- in MF_6^- is well known.

The electronic spectrum of the product obtained from the reaction between Te and $NOPF_6$ contains bands which could not be assigned by comparison with any known Te cations. When dissolved in 15% oleum, Te gives a red solution with an electronic spectrum λ_{max} 512 nm. As the strength of the oleum is increased the band shifts to 470 nm, these bands have been assigned to the Te_4^{2+} cation.[27] The initial species formed in the reaction between Te and MoF_6 in MeCN is red and the band position λ_{max} 445 nm can be tentatively assigned to Te_4^{2+}. This species then appears to undergo further oxidation, from $Te^{(\frac{1}{2})}$ to Te^{IV} resulting in a change in the electronic spectrum new bands being λ_{max} 320, 242 and 205 nm (Figure 5.3). In superacidic media[27] the following oxidations can occur, equations 3-4 which depend on the strength of the oxidising agents and the solvents used.

$$Te + \boxed{\begin{matrix} AsF_5 \\ SO_3 \\ SbF_5 \end{matrix}} \xrightarrow[\text{solvents}]{\boxed{\begin{matrix} \text{Oleum} \\ SO_2 \\ AsF_5 \end{matrix}}} Te_4^{2+} \qquad (3)$$

Oxidants

Red

$$3Te_4^{2+} + \text{oxidising agent} \longrightarrow 2Te_6^{4+} \qquad (4)$$

The oxidation of Te_6^{4+} to Te^{IV}, equation 5, does not appear to proceed in SO_2 or AsF_3 with AsF_5 or SbF_5 probably because they are not powerful enough oxidants, that is, it occurs only using strong oleum after several weeks.

$$Te_6^{4+} \xrightarrow[\text{strong oleum}]{\text{several weeks}} Te^{IV} \text{ colourless} \qquad (5)$$

There is no evidence for the oxidation of Te_6^{4+} to Te^{IV} by SO_3 in SO_2 although in oleum where SO_3 is the formal oxidant, oxidation is observed. This difference in behaviour which seems to be highly solvent dependent, could be kinetic in nature.

It appears that by using the strong oxidising agents UF_6 and MoF_6, the Te can be oxidised through to Te^{IV}. The MeCN molecules would be expected to solvate the bare Te^{IV} cation Te^{4+} but it appears that Te^{4+} is too polarising to exist simply as $Te(NCMe)_x^{4+}$ and fluoride transfer occurrs giving the cationic species $[TeF_3(NCMe)_2]^+$.

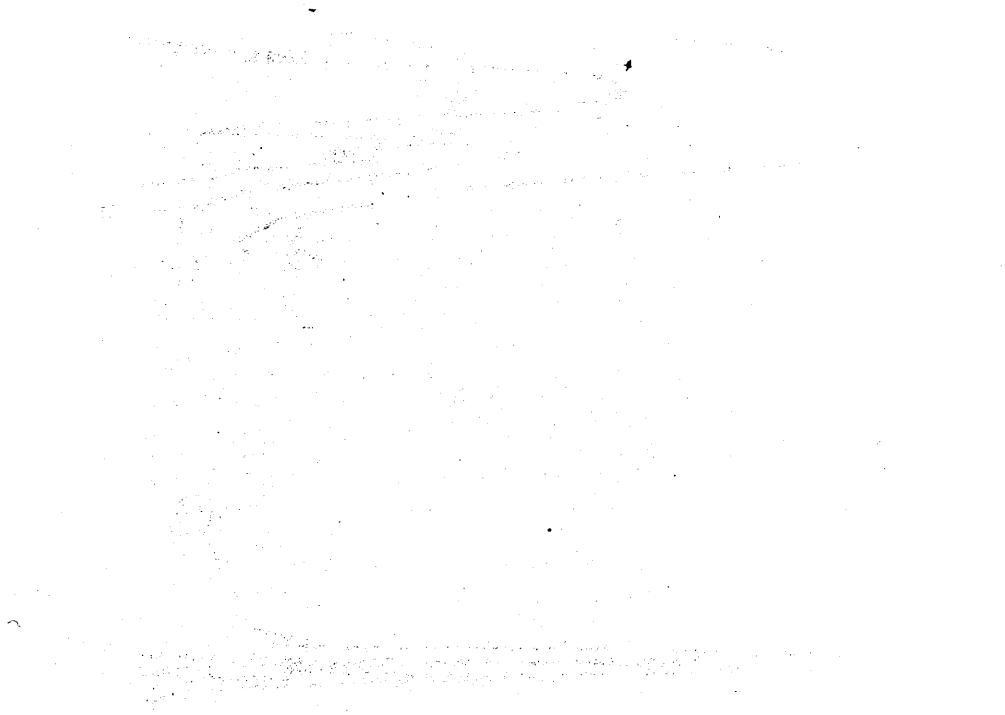
The formulation of the products as $[TeF_3(NCMe)_2][MF_6]$-$3MF_5NCMe$ where M = Mo or U, provides an explanation for most of the spectral features observed, and the analyses agree with this formula. Unfortunately no definitive evidence has been obtained for the cation $[TeF_3(NCMe)_2]^+$, but the existence of this species seems reasonable from the ^{125}Te n.m.r chemical shift data, the two metal fluoride species MF_6^- and MF_5NCMe present in each case and by

comparison with the known behaviour of $LTeF_4$ existing as $[L_2TeF_3^+][TeF_5^-]$. There is no direct evidence for $[TeF_3(NCMe)_2]^+$ from the vibrational spectra due to the complexity of the spectra. The Te-F stretches for the TeF_3^+ cation would be expected to appear where the other metal-fluoride stretches appear. However work undertaken by a colleague at the same time as the present work helped the interpretation of the infra-red spectra.[121] When molybdenum or tungsten metals are allowed to react in MeCN with molybdenum or tungsten hexafluorides, the adducts MF_5NCMe where M = Mo or W are obtained.[121] The vibrational spectra of these adducts aided the interpretation of the Te compounds vibrational spectra. The infrared spectra of $[TeF_3.2NCMe][MoF_6]3MoF_5NCMe$ and the pentafluoride adducts are compared in Table 5.8 and a composite figure of the spectra is shown in Figure 5.5.

Although SbF_5 and AsF_5 are strong oxidising agents in superacidic media[2], the adducts $SbF_5.NCMe$ and $AsF_5.NCMe$ are weak oxidising agents in acetonitrile, oxidising Te only to Te_4^{2+} and no further. The adduct AsF_5NCMe has previously been shown to exhibit no oxidising ability towards copper and silver metals in MeCN.[61] It was postulated that the reduction of AsF_5NCMe is thermodynamically unfavourable, or more likely the adduct is kinetically stable to reduction. The nitrosonium cation NO^+ has been shown to oxidise several metals in acetonitrile solution, releasing NO gas[36,122]. When the NO^+ cation was allowed to react with Te, the tellurium appeared to be oxidised to Te_4^{2+} giving a red species λ_{max} = 522 nm, further oxidation occurred which was followed by a change in λ_{max} position. A pure product could not be obtained from the solution and this precluded detailed examination

Table 5.8 Comparison of Pentafluoride Acetonitrile Adducts Vibrational Spectra with that of $[TeF_3(NCMe)_2][MoF_6]$-$3MoF_5NCMe$.

Infra red cm^{-1}					
$[TeF_3(NCMe)_2][MoF_6]3MoF_5NCMe$		MoF_5NCMe		WF_5NCMe	
722	comb	720	comb	720	comb
703	Mo-N str	703	Mo-N str	703	W-N str
650	$Mo-F_{axial}$	650	$Mo-F_{axial}$	640	$W-F_{axial}$
635	$[MoF_6]^-$ ν_3	635	$Mo-F_4$ eq str	610	WF_4 eq str
418	CCN def	418	CCN def	418	CCN def
290	$F-MoF_4$ def	285	$F-MoF_4$ def	270	$F-WF_4$ def
250	MoF_4 in plane def	250	MoF_4 in plane def	240	WF_4 in plane def



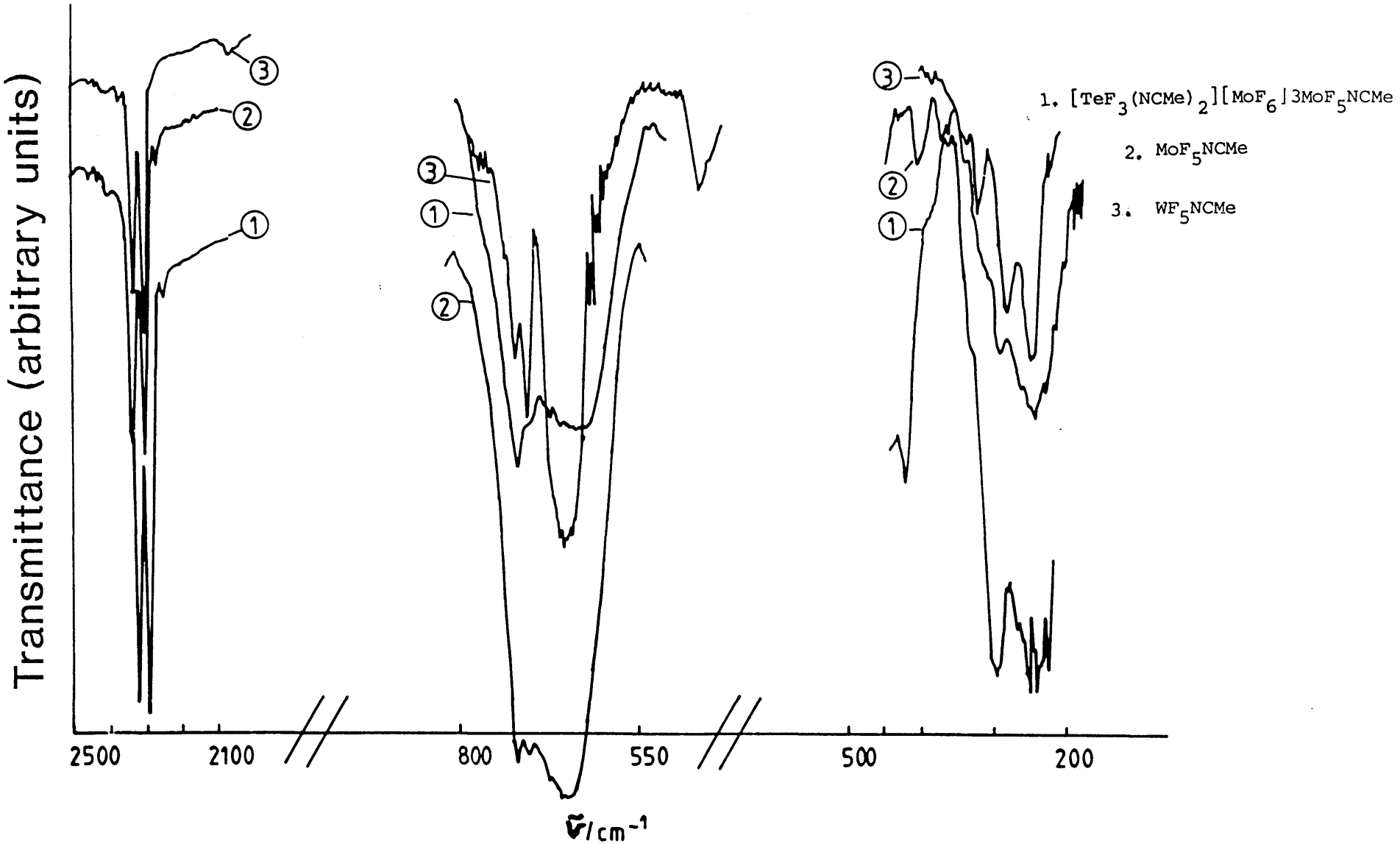

Transmittance (arbitrary units)
2500
2100
800
550
500
200
$\tilde{\nu}$/cm^{-1}
1. $[TeF_3(NCMe)_2][MoF_6]3MoF_5NCMe$
2. MoF_5NCMe
3. WF_5NCMe

Figure 5.5

of the NO^+ system.

A definitive answer to the structure of the Te compounds requires a crystal structure determination. Attempts to grow single crystals of the species $[TeF_3(NCMe)_2][MF_6]$ $3MF_5NCMe$ have been encouraging but to date unsuccessful.

EXPERIMENTAL

Unless described below, procedures for the purification of reagents, the manipulation of products and spectroscopic measurements were as described in Chapter 7.

Preparation of Arsenic Pentafluoride and its Acetonitrile Adduct.

The room temperature fluorination of arsenic metal was performed using the apparatus described in Chapter 7 for the preparation of molybdenum hexafluoride. Lumps of arsenic were placed in the nickel boat and fluorine:nitrogen 1:3 was flowed through the system. Colourless fumes were evolved and collected in trap E (break-seal vessel) at 153 K. The fluorine was passed for 45 minutes, followed by a nitrogen flow for 30 minutes; the apparatus was then removed to a vacuum line and the AsF_5 distilled onto fresh NaF and stored at 77 K.

The acetonitrile adduct was prepared by distilling AsF_5 (10 mmol) into a double limb vessel containing MeCN (10 cm^3), a colourless solution was obtained and removal of the volatiles left a colourless solid identified as AsF_5NCMe by its infrared spectrum.[123]

Preparation of $[TeF_3(NCMe)_2][MoF_6].3MoF_5.NCMe$

A piece of tellurium ingot (Specpure) was broken in an agate mortar and pestle and a small piece (0.25g, 1.96 mmol) added to a double limb vessel. Acetonitrile (5 cm^3) was distilled onto the Te followed by MoF_6 (10 mmol). When the mixture reached room temperature a pink colour was observed, this gradually changed to blood red after ca. 1 hour. Removal of the volatile material left an off-white solid formulated as $[TeF_3(NCMe)_2][MoF_6]$-$.3MoF_5.NCMe$, on the basis of its analyses, ^{125}Te n.m.r, vibrational and electronic spectra.

Analysis : Found C, 10.2; H, 1.2; F, 38.7; N, 5.9; Mo, 33.0; Te, 10.8%. $C_{10}H_{15}F_{24}N_5Mo_4Te$ requires C, 10.2; H, 1.3; F, 38.9; N, 6.0; Mo, 32.7; Te, 10.8%. The vibrational spectra of the solid are listed in Table 5.5 and Table 5.6. Its electronic spectrum in MeCN consisted of bands at ν_{max} 320, 242 and 205 nm (Figure 5.3).

Preparation of $[TeF_3(NCMe)_2][UF_6].3UF_5NCMe$.

This compound was prepared in the same manner as the molybdenum salt, using UF_6 as the oxidising agent. When the solution was allowed to warm to room temperature a light green colour was observed, and this gradually changed to a blue green solution. Removal of the volatile material left a pale green crystalline solid identified as $[TeF_3(NCMe)_2][UF_6].3UF_5NCMe$. Analysis : Found C, 6.9; H, 0.8; F, 26.0; N, 4.1; Te, 7.1; U 54.5% $C_{10}H_{15}F_{24}N_5TeU_4$ requires, C, 6.9; H, 0.9; F, 26.2; N, 4.0; Te, 7.3; U, 54.7%. Its vibrational (Table 5.1) and electronic spectra (Figure 5.1) are listed in the results section of this chapter.

Reaction of Tellurium with Nitrosonium Hexafluorophosphate in Acetonitrile.

A piece of Te (0.1 g, 0.8 mmol) was crushed and added to a double limb vessel, $NOPF_6$ (0.5 g, 2.8 mmol) was added to the other limb. Acetonitrile ($5 cm^3$) was distilled onto the $NOPF_6$, the solution was decanted onto the Te, bubbles of gas were released and a pink colour formed from the Te surface. The pink solution absorbed in the visible region at λ_{max} 522 nm assigned to Te_4^{2+}. Removal of the volatile material always left a sticky brown material, which could not be analysed.

Reaction of Tellurium with AsF_5NCMe and SbF_5NCMe in Acetonitrile.

A piece of Te (0.1 g, 0.8 mmol) was crushed and added to a double limb vessel, MF_5NCMe, M = Sb or As, (1 g 4.8 mmol) was added to the other limb. Acetonitrile (5 cm^3) was distilled onto the adduct and the resulting solution was decanted onto the Te. No immediate change was observed, a slight pink colour formed overnight with shaking. After one week the colour had darkened slightly. The solution had an absorption at λ_{max} 523 nm assigned to Te_4^{2+}. Removal of the volatile material left a pale pink solid identified by Raman and infrared[98] as a mixture of starting MF_5NCMe adduct and $[MF_6]^-$ anions.

$[SbF_6]^-$ ν_1 668, ν_3 669 cm^{-1}

$[AsF_6]^-$ ν_1 685, ν_3 699 cm^{-1}

CHAPTER SIX

ELECTROPHILIC BROMINATION OF AROMATIC COMPOUNDS USING $[Br(C_6H_9N_3)][UF_6]$ AND A COMPARISON WITH THE BEHAVIOUR OF NAFION HYPOHALITES AND $[Br_3][SbF_6]$.

Introduction

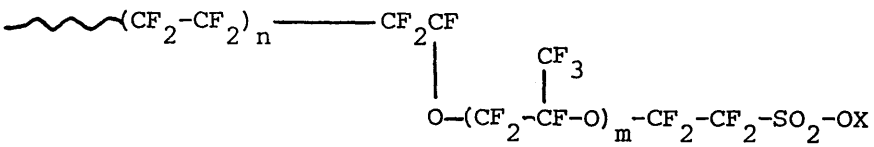
It has been shown that the salts $[I(NCMe)_2][MF_6]$ (where M = Mo or U) are good oxidising and iodinating agents in MeCN.[39] In chapter three the synthesis of the N-bromo compound $[Br(C_6H_9N_3)][UF_6]$ has been described, and it seemed worthwhile therefore to investigate the potential of this salt as a brominating agent. This work was undertaken as a project sponsored by 'The Associated Octel Co. Ltd.' with Gordon Haining as a co-worker. The objectives were to determine the scope of electrophilic bromination using $[Br(C_6H_9N_3)]^+$ as a reagent and then to compare the behaviour of $[Br(C_6H_9N_3)]^+$ with other materials containing electrophilic bromine. The salt $[Br_3][SbF_6]$ and the halogenated ion exchange resin Nafion-Br, were chosen as convenient "Br" sources. The salt $[Br_3][SbF_6]$ allowed comparisons to be made between the two electrophilic bromine containing salts, and Nafion-Br enabled comparison to be made with another type of "Br^+" species. The benefits of using reagents supported on ion exchange resins have been discussed in detail in the introductory chapter.

Electrophilic bromination of aromatic hydrocarbons is a well established procedure discussed in every elementary textbook.[46] However it often involves the aromatic molecule being subjected to severe conditions such as refluxing with bromine in oleum at high temperatures or it involves the use of Friedel-Crafts catalysts. These aluminium halide catalysts often lead to the loss of functional groups. For example, bromination of diphenyl sulphoxide, diphenyl sulphide or diphenyl methane with Br_2 in the presence of $AlBr_3$ gives hexabromobenzene.[129]

By using reagents containing electrophilic bromine, it was envisaged that brominations could be carried out at low temperatures without the use of catalysts. This would represent a saving in energy costs and should minimise unwanted decomposition of the organic material. If electrophilic bromine can be incorporated into an ion exchange resin, this will provide a synthetically useful reagent which will be easier to use in a practical sense than conventional brominating reagents.

Results of Bromination Reactions Involving $[Br(C_6H_9N_3)][UF_6]$, $[Br_3][SbF_6]$ and Nafion-Br.

Three sources of electrophilic bromine were used in this work. The salt $[Br(C_6H_9N_3)][UF_6]$ was prepared according to the method described in Chapter 3. The protonated form of the ion exchange resin Nafion, Nafion-H, was converted to Nafion-Br or Nafion-Cl according to the published procedures.[51] The structure proposed for the hypohalites is shown below.



(where X = Cl or Br).

The salt $[Br_3][SbF_6]$ was prepared by adding bromine *in vacuo* at room temperature to the salt $[O_2][SbF_6]$. After one hour the volatile material was removed; a chocolate brown solid was obtained analogous to $[Br_3][AsF_6]$ which is prepared by the action of Br_2 on $[O_2][AsF_6]$.[16] The $[Br_3]^+$ cation was identified by its electronic spectrum in SbF_5/HSO_3F, λ_{max} 375, 310 nm.

I. Reactions of $[Br(C_6H_9N_3)][UF_6]$ in MeCN

No attempt was made to separate the components of the mixtures formed nor to optimise yields, but examination of the products by mass spectrometry and ^1H n.m.r. spectroscopy enabled identification of the compounds to be achieved in most cases. The general technique used in the reactions involving the salt

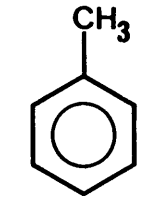
$[Br(C_6H_9N_3)][UF_6]$ was to weigh out the compound in the glove box. The weighed material was added to a solution of the organic material in MeCN at room temperature in the open air. The mixture was left for ca 1 hour, water was then added, which hydrolysed the $[UF_6]^-$ anion giving insoluble uranium oxides. The organic material was extracted with pet. ether, separated and dried using a nitrogen flow. The organic materials investigated are shown in Figure 6.1.

The Reactions of $[Br(C_6H_9N_3)][UF_6]$ in MeCN

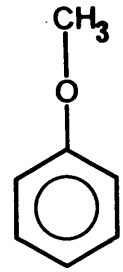
a) With Toluene : Colourless crystals were obtained, the mass spectrum shows incorporation of up to four bromine atoms into the ring system. The ^1H n.m.r. spectrum has a complicated splitting pattern in the aromatic region between 7.2 and 7.9 ppm which arises from dibromo and tribromo toluene. A singlet at 4.4 ppm may be due to $-CH_2Br$ and two singlets at 2.6 and 2.8 ppm were assigned to methyl groups.

b) With Anisole : Colourless needles were formed from the extracted organic layer overnight. Up to four bromine atoms were incorporated into the ring system, with good evidence for the formation of tribromoanisole. The ^1H n.m.r. spectrum contained a complicated pattern in the aromatic region between 6.7 and 7.9 ppm with singlets at 3.8, 4.3 and 4.4 ppm.

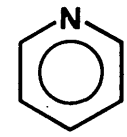
c) With 9-Methylanthracene : Release of bromine vapour was observed when the organic was added to the salt $[Br(C_6H_9N_3)][UF_6]$ in MeCN. The mass spectrum shows that incorporation of two bromine atoms



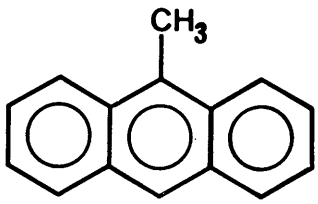
Toluene



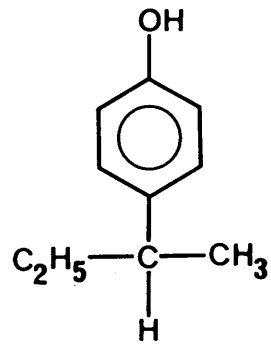
Anisole



Pyridine

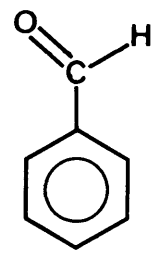


9-Methylanthracene

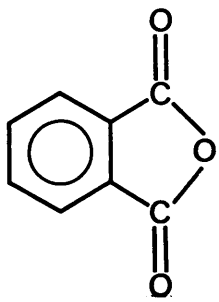


4-s-Butylphenol

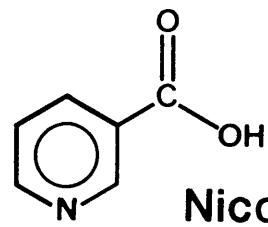
Pentafluorobenzene



Benzaldehyde



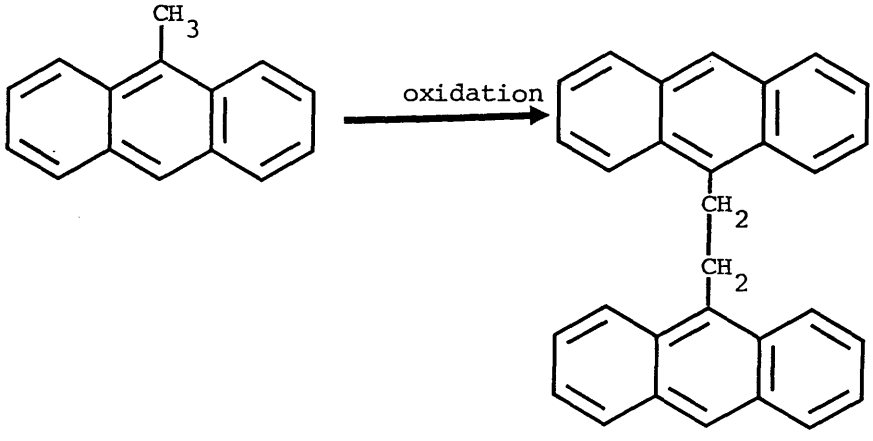
Phthalic Anhydride



Nicotinic Acid

Figure 6.1

into the 9-methylanthracene had occurred. The ^{1}H n.m.r spectrum in the aromatic region is complicated, but substitution appears to have taken place. Two methyl singlets at 2.6 and 3.1 ppm were observed, the singlet at 3.1 ppm was assigned to the starting material. Two singlets near 4.4 ppm were tentatively assigned to $-CH_2-$ groups in the dimer which is the normal product when 9-methylanthracene is oxidised.[130] It has been formulated as 1,2-bis(9-anthryl)ethane equation 1.



(1)

Dimerisation of 9-methylanthracene occurs when 9-methylanthracene is oxidised by benzoyl peroxide at 353 K in chlorobenzene and the authors suggest that it may occur via a free radical mechanism.[130]

d) With 4-s-butylphenol : A brown, viscous oil was isolated; its mass spectrum indicates that mono and dibromination had occurred. Two peaks at m/z 199 and 201 (intensities 13.4 and 14.1) were assigned to a monobrominated ion from which the C_2H_5 side chain had been lost. There is a triplet of peaks at m/z 277, 279 and 281 (intensities 1.4, 2.9, 1.8) which corresponds to a dibrominated ion without the C_2H_5 sidechain. The ^{1}H n.m.r spectrum indicates that bromination had occurred in the allylic position, and the

splitting of the aromatic signals indicates that bromination of the ring had taken place.

e) With Benzaldehyde : Wet, yellowish crystals were obtained; their mass spectrum contains evidence for three bromine atoms incorporated into benzaldehyde. A doublet at m/z 154 and 156 (int. 11.6, 10.5) corresponds to a monobrominated product ion that has lost the $\overset{O}{\overset{\|}{C}}-H$ group. A triplet at m/z = 262, 264 and 266 (int. 8.3, 15.7, 7.5) corresponds to the dibrominated molecular ion of benzaldehyde. A quartet at m/z 340, 342, 344, 346 (intensities 0.4, 1.3, 1.1, 0.4) indicates an ion corresponding to the incorporation of three bromine atoms into benzaldehyde. This reaction was repeated using the same conditions and brominated benzoic acid was obtained. A quartet at m/z 363, 361, 359, 351 (intensities 2.9, 9.1, 9.1, 3.1) indicates that three bromine atoms were incorporated into the benzoic acid. A triplet at m/z 282, 280, 278 (int. 17.2, 33.9, 17.4) indicates that two bromine atoms have been incorporated in benzoic acid and a doublet at m/z 202, 200 (int. 9.4, 10.7) indicates mono-brominated benzoic acid. The aromatic region of the ^{1}H n.m.r spectrum indicates that two types of aromatic product were present in the brominated benzaldehyde.

f) With Nicotinic Acid : An off-white solid was obtained. There is clear evidence for monobromination and a little di and tribromination. The mass spectral patterns are m/z 201, 203 (int. 14.9, 14.0), m/z 278, 280, 282 (int. 3.5, 7.0, 3.5) m/z 279, 281, 283 (int. 4.4, 8.6, 4.2) and m/z 357, 359, 361, 363 (int. 0.4, 1.2, 1.2, 0.3).

g) With Pyridine : A yellow oil was isolated, and from its mass spectrum it is apparent that three atoms of bromine were incorporated into the molecule. However it is not a brominated pyridine derivative as the masses of the peaks are too high. The brominated fragments are as follows, monobrominated m/z 159, 161 (int. 14.6, 11.3) dibrominated m/z 278, 280, 282 (int. 11.2, 22.2, 11.0) tribrominated m/z 356, 358, 360, 362 (int. 19.0, 57.4, 57.3, 18.6).

h) With Phthalic Anhydride : An off-white solid was obtained which does not appear to be brominated from its mass spectrum. Phthalic anhydride although insoluble in acetonitrile, immediately goes into solution when $[Br(C_6H_9N_3)][UF_6]$ is added, and the observations suggest that a reaction is occurring.

i) With Pentafluorobenzene : No bromination appears to have occurred, that is no reaction was observed.

II. Reactions of $[Br_3][SbF_6]$ with organics dissolved in carbon tetrachloride.

Samples of $[Br_3][SbF_6]$ were weighed in the glove box and removed in sealed sample bottles. The organic component was dissolved in carbon tetrachloride and added to the salt $[Br_3][SbF_6]$ at room temperature in the open air. After 30 minutes, water was added to hydrolyse the salt; and the organic material was extracted and dried by blowing nitrogen over the surface.

Reactions of the salt $[Br_3][SbF_6]$

a) With 4-s-butylphenol : A brown viscous oil was isolated, which shows evidence for monobromination, m/z 199, 201 (int. 26.3, 21.1) dibromination a triplet m/z 277, 279, 281 (int. 22.8, 34.1, 17.7) and tribromination m/z 354, 356, 358, 360 (int. 5.2, 16.4, 16.4, 5.2). As mentioned earlier the m/z values of these peaks are consistent with fragments of the molecular ion which has lost the C_2H_5 side chain. The ^1H n.m.r. spectrum in the aromatic region is shifted downfield by 0.3 ppm consistent with the incorporation of bromine into the ring. The allylic proton signal also decreased in intensity compared with the starting material allylic proton signal suggesting that bromination of the allylic proton had occurred.

b) With Benzaldehyde : A pale yellow solid was obtained, which shows bromination has occurred. Monobromination m/z 184, 186 (int. 8.1, 7.5) due to molecular ion and one bromine, dibromination m/z 261, 263, 265 (int. 2.2, 4.8, 2.5) and tribromination m/z 340, 342, 344, 346 (int. 0.5, 1.5, 1.6, 0.4). The ^1H n.m.r spectrum shows two distinct aldehydic proton signals at 9.95 and 10.25 ppm.

c) With Pyridine : Although the mass spectrum shows peaks of high mass (up to 488) very little evidence of bromination was found.

d) With Nicotinic Acid : An off white solid was obtained which appears to be brominated, a doublet at m/z 156 and 158 (int. 27.1, 28.5) corresponds to monobrominated nicotinic acid with the loss of the COOH group. However the molecular ion peaks that should

appear at m/z 199 and 201 were not observed in the spectrum. Therefore it can only be said that bromination may have occurred.

e) With Pentafluorobenzene : Although the mass spectrum of the liquid contained very high mass values (m/z 443) no evidence for bromination was found.

III. Reactions of Nafion Bromide with Organics dissolved in Carbon Tetrachloride.

a) With 4-s-butylphenol : A brown viscous oil was obtained; the mass spectrum shows evidence for incorporation of three bromines into the molecule. A doublet m/z 199, 201 (int 21.2, 21.1) is due to the incorporation of a bromine atom. A triplet m/z 277, 279, 231 (int. 3.5, 7.0, 3.8) corresponds to dibromination and a quartet m/z 355, 357, 359, 361 (int. 1.0, 3.6, 3.4, 1.2) corresponds to tri-bromination. These fragments are all derived from the molecular ion in which the C_2H_5 group has been lost.

b) With Benzaldehyde : Colourless crystals were obtained, from their mass spectrum, they appear to be benzoic acid and there is no evidence for bromination.

c) With Toluene : No reaction occurred, toluene was recovered unchanged.

Oxidising Properties of Halogenated Nafion.

The acidity and oxidising power of Nafion resins and the Nafion hypohalites that were synthesised were assessed by iodimetric and acid/base titrations.

i) Acid/base titrations of Nafion-H : Titrations of Nafion-H were carried out to determine the number of available H^+ ions that were present in the resin, expressed as mmol g^{-1}. The average H^+ value found for Nafion powder and beads was 0.9 mmol g^{-1}. The acidity of the resin appears to be completely neutralised after two hours shaking in excess sodium hydroxide solution.

ii) Iodimetric titration of Nafion-Br : Nafion-Br was added to excess Kl solution and the amount of iodine released was titrated with standard sodium thiosulphate solution. The Nafion-Br was titrated over a period of approximately 8 hours due to the slow release of iodine with time. The final value for available "Br^+" was 0.9 mmol g^{-1}.

iii) Iodimetric titrations of Nafion-Cl : Nafion-Cl was titrated using the same procedure for the Nafion-Br. The Nafion-Cl released iodine from solution relatively slowly. After 3 hours approximately 70% of the oxidising ability was released. Thereafter the iodine was released slowly for up to 24 hours. The final value for available "Cl^+" was 1.35 mmol g^{-1}. When a sample of Nafion-Cl was left exposed to the atmosphere overnight before iodimetry, the value obtained for its oxidising ability was 0.4 mmol g^{-1}.

Reaction of Nafion-Cl with Bromine in Acetonitrile.

Excess acetonitrile (3 cm^3) and bromine (2 cm^3) were added to Nafion-Cl and the mixture left to react at room temperature for two hours. During the first hour gas bubbles were evolved from the resin. When the volatiles were removed from the resin it had changed from white to a bright orange colour. This resin was titrated in KI solution using sodium thiosulphate. The iodine was released slowly from solution, 9 days were required for complete reaction to occur. The iodine appeared to be liberated almost uniformly throughout this time period. A final value of 0.38 mmol g^{-1} available "Br^+" (or oxidising material) was obtained.

Discussion.

The salt $[Br(C_6H_9N_3)][UF_6]$ proved to be the best brominating agent towards the organic compounds examined. Brominations performed at room temperature appear to be instantaneous. Although the radioactive anion $[UF_6]^-$, presents problems in the work-up and disposal procedures, with a little care these problems can be overcome and the benefits of the cation can be exploited relatively easily. The salt $[Br(C_6H_9N_3)][UF_6]$ has already been shown (Chapter 3) to be a good oxidising agent, for example it oxidises I_2 to I^+, NO gas to NO^+ and the solvated Cu^I ion to solvated Cu^{II}. Oxidation of the organic in addition to bromination was observed in some cases. Benzaldehyde is oxidised to benzoic acid which is subsequently brominated. The compound 9-methylanthracene undergoes dimerisation to give 1,2-bis(9-anthryl) ethane, evidence for this product being obtained from its mass spectra. When the salt $[Br(C_6H_9N_3)][UF_6]$ is added to 9-methyl-anthracene, bromine is observed being released; this amplifies the oxidative coupling argument proposed by other authors.[132]

The compound $[Br_3][SbF_6]$brominates some activated and mildly deactivated ring systems, but the reactions are exothermic and not easily controlled using the simple procedure adopted in this study. From the mass spectra, fragmentation of the organic molecules is observed which occurred from the bromination reaction, this fragmentation results in numerous low m/z values. The compound $[Br_3][SbF_6]$ is very easy to synthesise, but this appears to be its only benefit as a reagent under the conditions used here.

A cation exchange resin such as Nafion in which the H^+ has been replaced by Br^+ could provide a reagent with desireable synthetic properties. However Nafion-Br appears to be a poor brominating agent under the conditions used in this study. The release of "Br^+" from the resin is very slow even in aqueous solution. This is likely to be the reason why no bromination is observed. The Nafion-Br acts as an oxidising agent towards benzaldehyde giving benzoic acid as a product. This suggests that a positive bromine species is present but that it may be too tightly bound or inaccessible within the polymer for the resin to be effective as a brominating agent. Positive bromine species are known to be good oxidising agents, for example the salt $[Br(C_6H_9N_3)][UF_6]$.[83] Another example is bis(quinuclidine)bromine(I) tetrafluoroborate which in the presence of silver(I) tetrafluoroborate has been used to oxidise alcohols to carbonyl compounds, particularly secondary alcohols to ketones.[56] When bromine in acetonitrile was added to Nafion-Cl, the orange solid obtained discharged its "oxidising power" very slowly but uniformly over nine days. Nafion resins swell when in contact with solvents[50] and as a result bromine may be trapped within the polymer. The solvent MeCN is an important factor in this reaction since reaction does not occur between Nafion-Cl and Br_2 in the absence of the solvent. Previous work involving Nafion-Br is consistent with its formulation as a polymer containing R_F-SO_2OBr groups,[50] where R_F represents the fluorocarbonether backbone and side chains. Bromine in the SO_2OBr moiety is expected to be electrophilic and to exhibit oxidising behaviour since formally it exists in the (+1) oxidation state. The results from this study are not inconsistent with

this view but they demonstrate that the release of bromine is determined not by thermodynamic considerations, for example the weak O-Br bond, but by kinetic factors. The incorporation of bromine in the Nafion-Cl in the presence of MeCN, and its subsequent very slow release is a phenomenon that may have a similar explanation.

EXPERIMENTAL.

Unless described below, procedures for purification of reagents, manipulation of products and spectroscopic measurements were as described in Chapter 7.

Mass spectra were obtained using a Kratos M.12 spectrometer. Where possible the organic starting material was recorded as a reference. ^{1}H n.m.r spectra were obtained using a P.E. R32 spectrometer at 90 MHz (δ_H with respect to Me_4Si).

Reagents used were as follows:-

Bromine, pyridine, toluene, petroleum-ether 40^{o}-60^{o} (BDH AnalaR) pentafluorobenzene, 4-s-butylphenol, phthalic anhydride, Nafion NR50 beads, Nafion powder 35-60 mesh (Aldrich), benzaldehyde, carbon tetrachloride (May and Baker), chlorine (Matheson), $[O_2][SbF_6]$ and ClF_3 (Ozark Mahoning). These were all used as supplied.

Preparation of electrophilic bromine containing compounds.

The preparation of $[Br(C_6H_9N_3)][UF_6]$ was described in Chapter 3. The preparation of $[Br_3][SbF_6]$ was carried out as follows:-

$$Br_2(\text{excess}) + [O_2][SbF_6] \longrightarrow [Br_3][SbF_6] + O_2 \qquad (2)$$

Excess bromine was distilled onto 0.5g (1.9 mmol) $[O_2][SbF_6]$ and the mixture allowed to reach room temperature. The solution was degassed and the volatile material removed. A chocolate brown solid was left and the cation $[Br_3]^+$ identified by its electronic spectrum in SbF_5/HSO_3F λ_{max} 375, 310 nm.[16]

Preparation of Nafion Hypohalites.

The method used to prepare the Nafion hypohalites has been published by Desmarteau; [51] they were made as follows:

$$\text{Nafion H} \xrightarrow[\text{ClF 18 hrs}]{\text{193 to 243 K}} \text{Nafion Cl} \xrightarrow[\text{BrCl}]{\text{243-273 K}} \text{Nafion Br}$$

Chlorinemonofluoride (1.5 mmol) was added to 0.3g Nafion H in an FEP tube, at 77 K. The mixture was left overnight and the temperature rose from 193 K to 243 K. After 18 hours the volatile material was removed and a pale yellow material was obtained, Nafion-Cl. Equimolar amounts of bromine and chlorine were then added ca (1.5 mmol) and the mixture allowed to warm from 243 K to 273 K. Removal of the volatile material after 18 hours left an orange solid, Nafion-Br.

Reactions Involving $[Br(C_6H_9N_3)][UF_6]$

The general technique used in the bromination reactions involving $[Br(C_6H_9N_3)][UF_6]$ was to weigh out ca 0.5g (0.9 mmol) of the salt in the glove box. This was added to a solution of the organic compound in MeCN at room temperature in the open air. The mixture was left for ca 1 hour, then water was added to hydrolyse the $[UF_6]^-$ giving green insoluble uranium oxides. Carbon tetrachloride or 40-60° petroleum-ether were used to extract the organic components from the reaction mixture. The organic layer was separated, dried with anhydrous $MgSO_4$ and the solvent

removed by blowing a stream of nitrogen gas over the surface. The quantities of organic material used are given in Table 6.1.

Reactions of $[Br_3][SbF_6]$ with organics.

Samples of $[Br_3][SbF_6]$ were weighed in the glove box and removed in sealed bottles. The organic sample was dissolved in CCl_4 (5 cm^3) and added to the $[Br_3][SbF_6]$ Table 6.2. Heat and white fumes were liberated immediately from the mixture and a thick white precipitate formed. The solution turns reddish, presumably due to release of bromine. After two hours, water was added to complete the hydrolysis of the $[Br_3][SbF_6]$. The organic layer was separated, filtered, dried with $MgSO_4$ and the solvent removed by blowing nitrogen over the surface.

Reactions of Nafion Bromide.

a) With 4-s-butylphenol : Nafion-Br (0.3g) was added to a solution of 4-s-butylphenol (0.102g, 0.68 mmol) in CCl_4 (3 cm^3). After 18 hours shaking, the resin was filtered and the resulting solution evaporated giving a brown oil.

b) With Benzaldehyde : The organic (0.1 ml, 0.98 mmol) was dissolved in CCl_4 (3 cm^3) and added to Nafion-Br (0.4g). This was shaken for 18 hours and the resin filtered from the solution. The solvent was removed by nitrogen flow, and white crystals were obtained.

Table 6.1

Organic Reagent	Quantity (mmol)
Toluene	1.0
Anisole	1.0
9-Methylanthracene	0.8
4-s-butylphenol	0.7
Pentafluorobenzene	0.9
Benzaldehyde	1.0
Pyridine	1.25
Nicotinic Acid	0.8
Phthalic Anhydride	0.9

Table 6.2

Organic Reagent	Amount (mmol)		$[Br_3][SbF_6]$ (mmol)	
4-s-butylphenol	0.33	(0.049g)	0.6	(0.28g)
Pentafluorobenzene	0.9	(0.1 ml)	1.26	(0.6g)
Benzaldehyde	1	(0.1 ml)	1.35	(0.64g)
Pyridine	1.25	(0.1 ml)	1.18	(0.56g)
Nicotinic Acid	1.7	(0.21g)	1.47	(0.7g)

Table 6.3 Concentrations Used.

NaOH	HCl
0.04 M	0.1 M
0.39 M	0.4 M
0.4 M	0.1 M

c) With Toluene : Toluene (0.5 cm^3) was vacuum distilled onto Nafion-Br (0.3g) and left for 18 hours. The Nafion was removed by filtration and the solvent evaporated. The solution left was unreacted toluene.

Oxidising Properties of Nafion Hypohalites.

Acid/Base Titrations

Nafion H (powder or beads) was weighed in the glove box (ca 0.5g) in a sealed bottle. This was weighed accurately and the Nafion H added to 25.0 ml of standard sodium hydroxide solution (0.39 Molar) contained in a stoppered conical flask. This was shaken for two hours, and the solution back-titrated using standard HCl solution with phenophthalein as indicator. Concentrations of acid and base were varied, but each gave the same value for H^+ content of the resin, (Table 6.3).

Iodimetric Titrations of Nafion Hypohalites.

The Nafion hypohalite was stored at 77 K until required. For analysis it was weighed and added to a stoppered conical flask containing KI solution, as quickly as possible. The Nafion Hypohalite was still cold when entering the KI solution, this should have minimised any halogen release prior to reaction with KI. The mixture was shaken and left for varying times to liberate iodine. The liberated iodine was titrated using a standard sodium thiosulphate solution.

The available oxidising abilities of the resins were

calculated assuming the following reaction scheme equation 3.

$$\text{Nafion } X^{+} \xrightarrow{I^{-}} X \xrightarrow{I^{-}} X^{-} + I_2 \qquad (3)$$

$$\therefore \text{ 1 mole } I_2 \equiv \text{ 1 mole } X^{+} \qquad (X = Cl, Br)$$

In a typical measurement 0.2020g of Nafion Br was added to 0.5g (excess) KI in aqueous solution. The iodine liberated was then titrated with 0.1 M $Na_2S_2O_3$. 3.60 ml of $Na_2S_2O_3$ were required to oxidise all the I_2 present. The amount of available "Br" was therefore 0.9 mmol g^{-1}.

CHAPTER SEVEN

GENERAL EXPERIMENTAL TECHNIQUES.

Purification of Acetonitrile

As described in Chapter 1 acetonitrile is a useful solvent for work involving high oxidation state fluorides. Before it can be used however, it has to be rigorously purified; this purification is necessary to remove moisture and impurities such as acrylonitrile and benzene. A method has been developed in this Department[41] which is an extension of the method published by Walter and Ramalay.[133] Acetonitrile (H.P.L.C. Grade, Rathburn Chemicals Ltd.) was refluxed several times in a Pyrex still equipped with a 0.75m vacuum-jacketed separating column, which was protected from atmospheric moisture by silica-gel drying tubes. The following sequence of reagents is used, quantities and times are given in parentheses:

i) anhydrous $AlCl_3$ (15 g dm^{-3}; 1h)

ii) $KMnO_4$ + Li_2CO_3 (10 g dm^{-3} each, 0.25h)

iii) $KHSO_4$ (15 g dm^{-3}, 1h)

iv) CaH_2 (20 g dm^{-3}, 1h)

v and vi) P_2O_5 (1 g dm^{-3}, 0.5h)

The solvent was rapidly distilled and topped and tailed by approximately 3% after each reflux. The distilled acetonitrile was collected after the final stage in vessels containing activated alumina (neutral 60 mesh), degassed twice *in vacuo* and distilled onto activated 3 Å molecular sieves. The purified MeCN had an absorbance of less than 0.05 (H_2O reference) at 200 nm and an apparent U.V. cut-off point *ca.* 175 nm.

Vacuum Line and Glove Box Techniques

In order to ensure anhydrous and oxygen free conditions, all experimental work involving air sensitive compounds was carried out in Pyrex or Monel metal vacuum lines, and a nitrogen atmosphere glove box (Lintott Engineering) in which H_2O < 5 p.p.m.

Conventional high vacuum techniques were used throughout this work. A rotary oil pump (Edwards high vacuum or Genevac) in series with a mercury diffusion pump (Jencons) provided a vacuum of 10^{-4} Torr. Standard glass joints were greased with Apiezon N or Voltalef Kel-F high vacuum greases. Semi-permanent joints were sealed with Apiezon black wax. Polytetrafluoroethylene (P.T.F.E.) Pyrex stop-cocks (Rotaflo or J. Young) were used when required. Reactions were carried out in double limbed vessels (Fig. 7.1) fitted with Rotaflo or J. Young P.T.F.E. stopcocks. Similar vessels with one limb replaced by an n.m.r. tube, Pyrex capillary for Raman or Spectrosil cell for electronic spectroscopy were used when required. All glassware was well flamed out before use.

Double limbed vessel

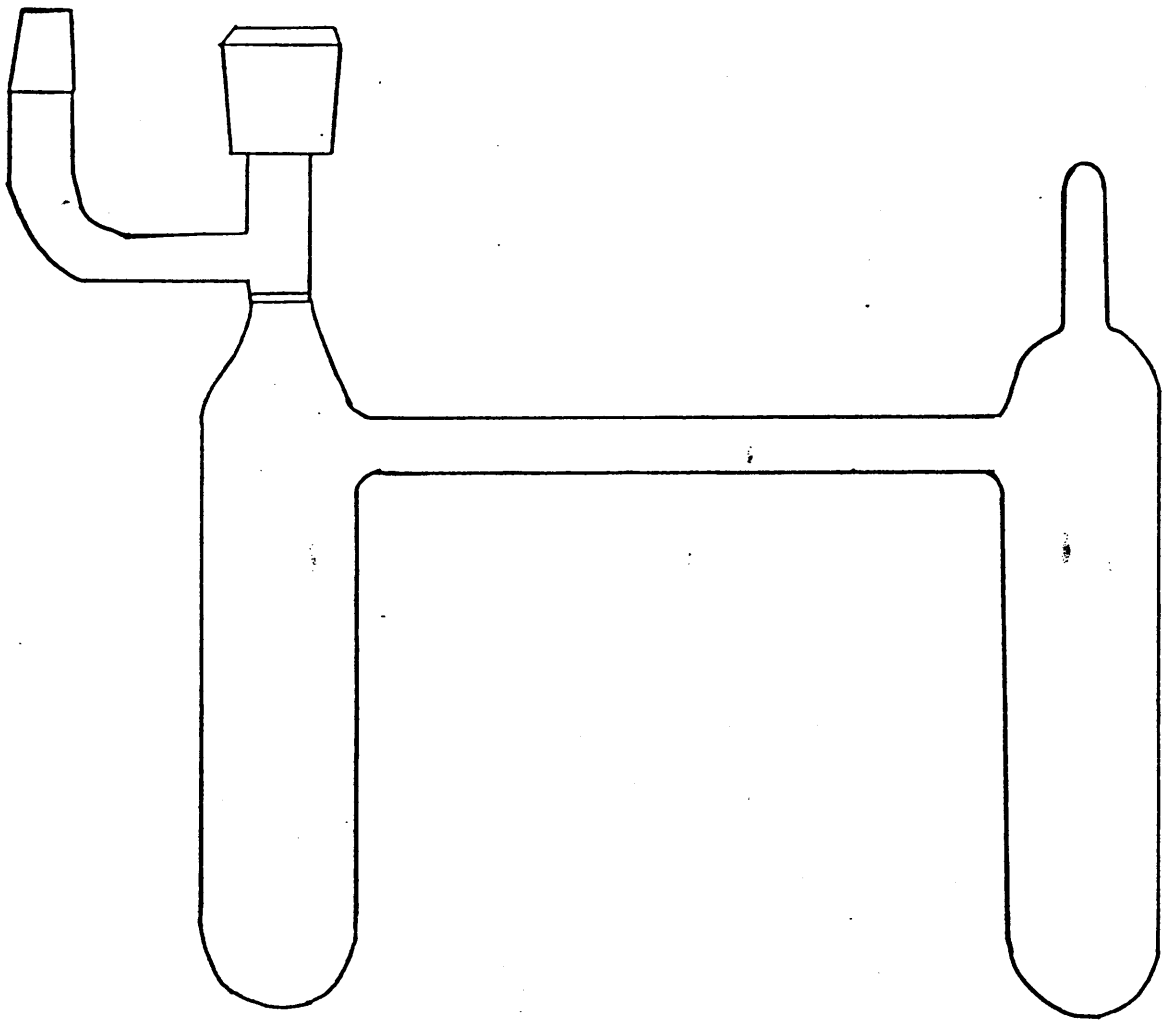


Figure 7.1

Preparation of Molybdenum Hexafluoride.

Molybdenum hexafluoride can be prepared by several methods such as fluorination of the hexavalent oxide, with bromine trifluoride sulphur tetrafluoride, or hydrogen fluoride, [134] or by direct combination of the elements at high temperature. [135] The method employed at Glasgow involved fluorination of powdered molybdenum metal with elemental fluorine at 573 - 623 K. By excluding moisture and by trapping HF with NaF, Pyrex glass can be used for the preparation.

Procedure : Powdered molybdenum (5 g) was placed in a nickel boat, this was placed inside the large nickel pipe, connections were made to the glass apparatus by P.T.F.E. ferrules and Swagelok couplings. The assembly (Fig. 7.2) was evacuated and all the glassware flamed out. Nitrogen gas was admitted to the system, excluding atmospheric moisture at all times. Cold traps were then placed around trap C, (trapping moisture from air), traps F and G (for collecting product MoF_6) and trap I (for trapping HF). The traps were cooled with dry ice/dichloromethane slush baths at 193 K. The oven was then switched on and when a temperature of ca. 623 K was reached fluorine was admitted to the system diluted in the nitrogen flow by a ratio of 1:2. After 5 minutes of fluorine flow the oven was switched off as the reaction is exothermic. When the reaction was complete, the fluorine was stopped but nitrogen flow continued for a further 15 minutes. The glass apparatus was then sealed at point H using a gas/oxygen torch and the collection train (b) attached to a vacuum line. The product was frozen at 77 K and the manifold

Apparatus for the preparation of Molybdenum Hexafluoride.

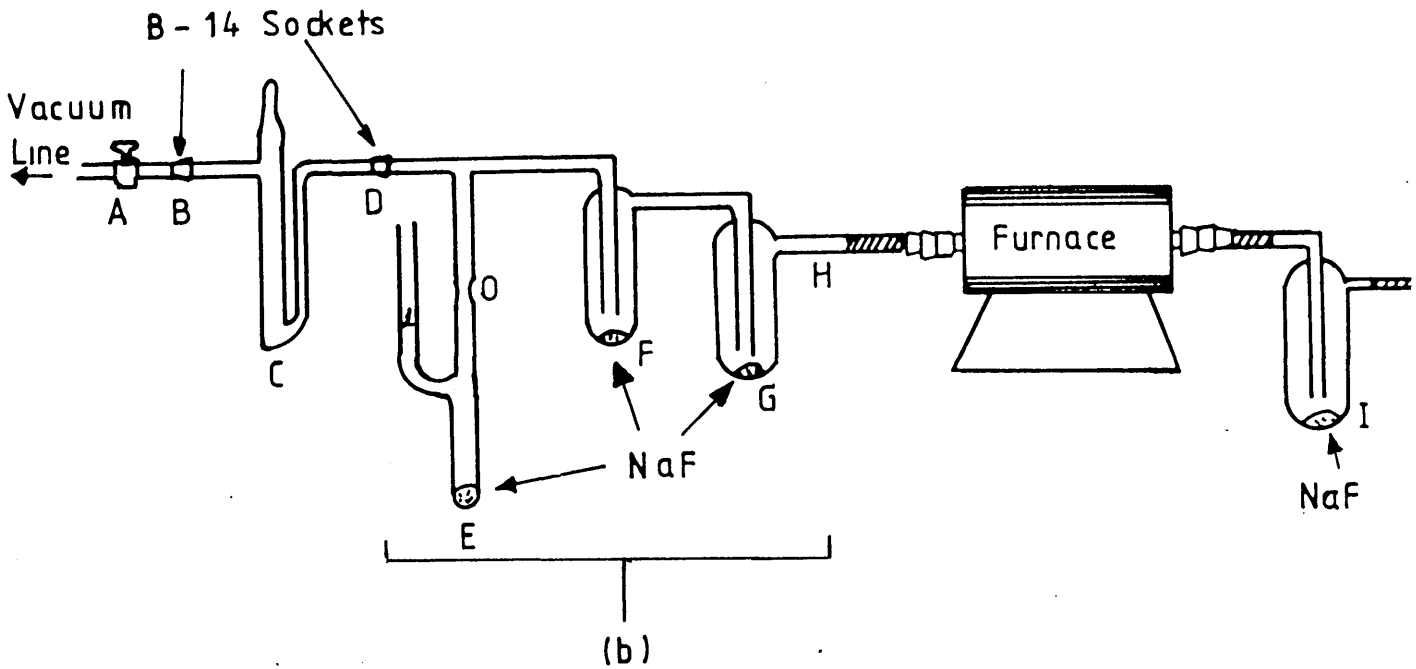


Figure 7.2

(b) evacuated. The product MoF_6 was purified by trap to trap distillation. The product was finally stored in a break seal ampoule (E) and kept in liquid nitrogen until required.

Extended X-ray Absorption Fine Structure (EXAFS) Spectroscopy.[136,137]

Extended X-ray absorption fine structure (EXAFS) spectroscopy refers to the sinusoidal variation of the X-ray absorption as a function of photon energy beyond an absorption edge. By monitoring the attenuation of X-rays through a material the absorption coefficient (μ) can be measured. If the photon energy (E) is tuned to the binding energy of some core level of an atom of interest in the sample, a sharp increase in μ known as the absorption edge occurs. In isolated atoms μ would decrease monotonically as a function of E beyond the edge. For molecules, solids, solutions or matrices, the variation of μ of energies above the absorption edge displays a fine structure named EXAFS, (Figure 7.3).

$$\mu X = \ell n\ I_o/I \qquad (1)$$

where

μ = absorption coefficient

X = thickness of sample

I_o = incident X-ray beam

I = transmitted X-ray beam

EXAFS is caused by backscattering of the ejected photo-electron from neighbouring atoms. This fine structure has been known for more than fifty years. It is only in the past decade, however, that useful information could be extracted from the post-edge region. The reason is that a spectrum clear enough to show the fine detail required needs an intense beam of X-rays. This intense source of X-rays is provided by synchrotron

Plot of Photon energy E versus μx (absorbance)

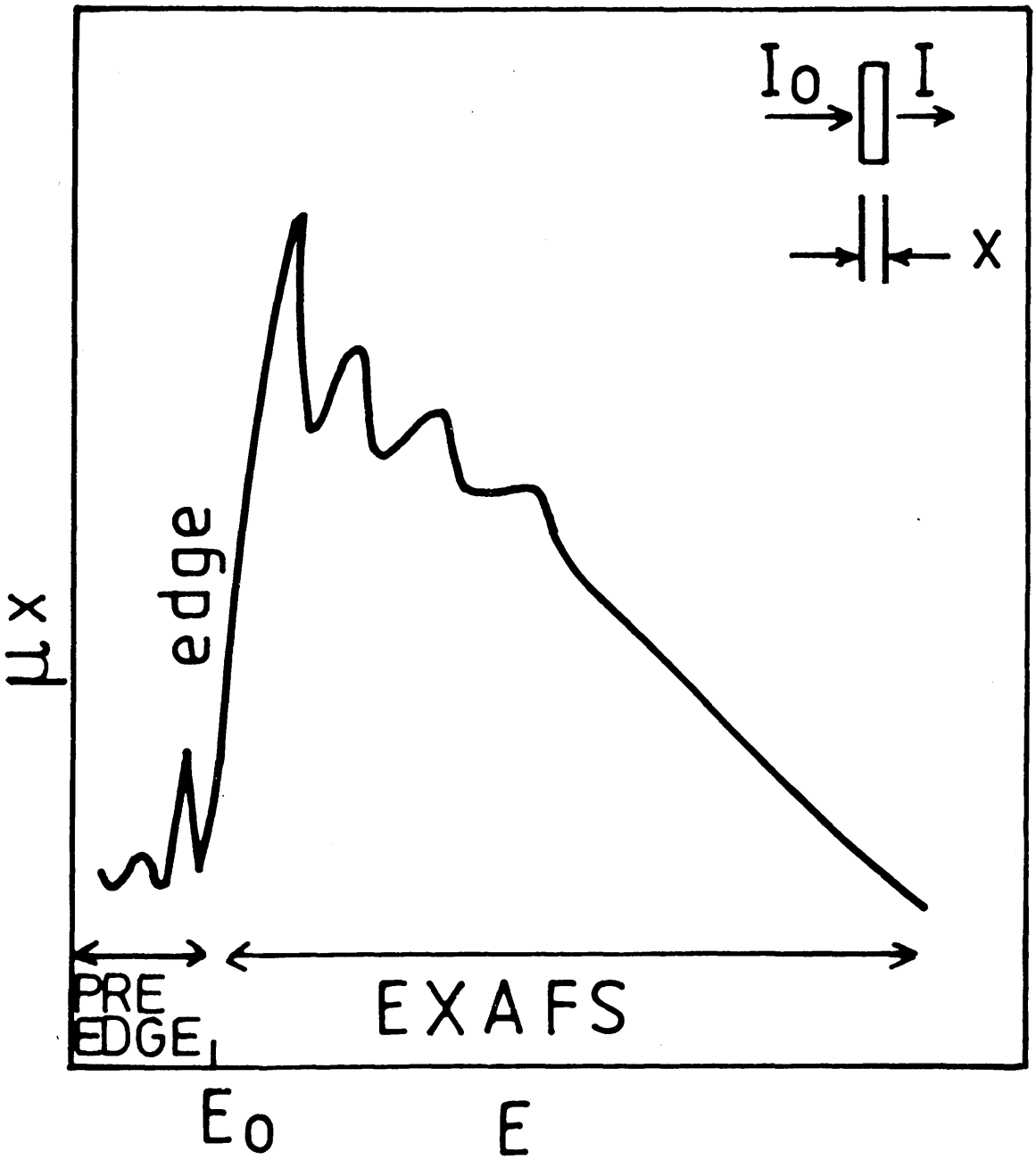


Figure 7.3

radiation.

In understanding EXAFS, it is easier to think of electrons as waves, these waves can cancel or reinforce each other depending on the phase. An electron can be backscattered by a neighbouring atom, the reflected wave can then enhance the X-ray absorption or reduce it. It is therefore possible to interpret the intensity and frequency of EXAFS in terms of the number, nature and distance of backscattering atoms next to or near to the absorber (Fig. 7.4). This leads to information about the molecular environment. The advantages and disadvantages of EXAFS are summarised in Table 7.1.

Analysis of EXAFS and data reduction

The analysis of the EXAFS spectrum is carried out using dedicated computer software. The first stage in data reduction is the removal of background and extraction of the EXAFS data, and its normalisation to unit metal atom. The pre-edge is subtracted by fitting a linear quadratic function, this function is extrapolated over the whole range of the experimental spectrum. The post-edge resulting from a variation in atomic absorption is removed by fitting a pair of polynomials, whose positions are chosen where the EXAFS oscillations become small (Fig. 7.5). Removal of these parameters leads to a normalised EXAFS spectrum being produced (Fig. 7.6). A Fourier Transform is then performed on the normalised spectrum (Fig. 7.7) which shows peaks due to various scattering distances. The flow chart (Fig. 7.8)

Physical Origins of EXAFS.

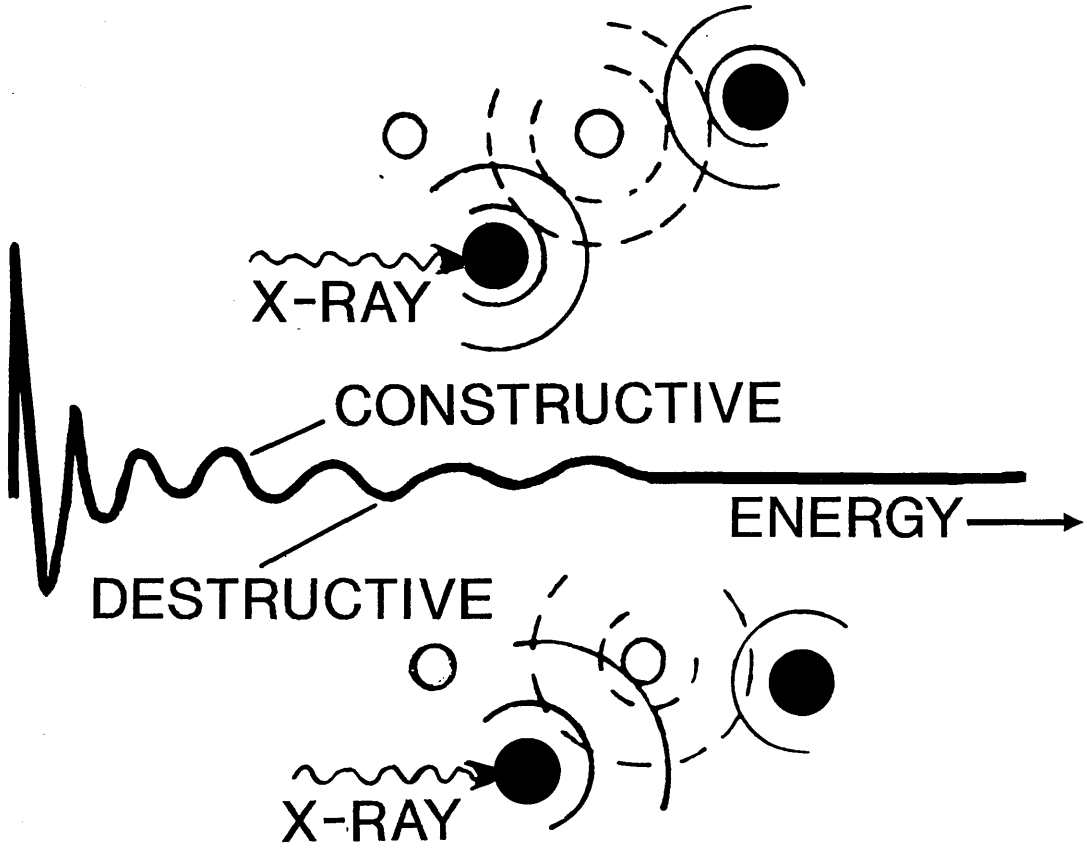


Figure 7.4

Table 7.1 Advantages and Disadvantages of EXAFS.

Advantages

1. No single crystal required.
2. Element specific for virtually all elements.
3. Good contrast of X-ray absorption over background 1 atom in 10^6 obtained.
4. Accurate interatomic distances, $\pm$ 0.02 Å within 3.5 Å of primary absorber.
5. Studies as a function of time are possible.

Disadvantages

1. No angular information obtained.
2. Data restricted to < 3.5 Å.
3. Possibility of radiation damage.
4. Validity of interpretation involves the adjustment of several parameters within a theoretical model to reproduce the experimental data.

Absorption spectrum showing the pre(1) and post(2) edge polynomials used for the background subtraction programme.

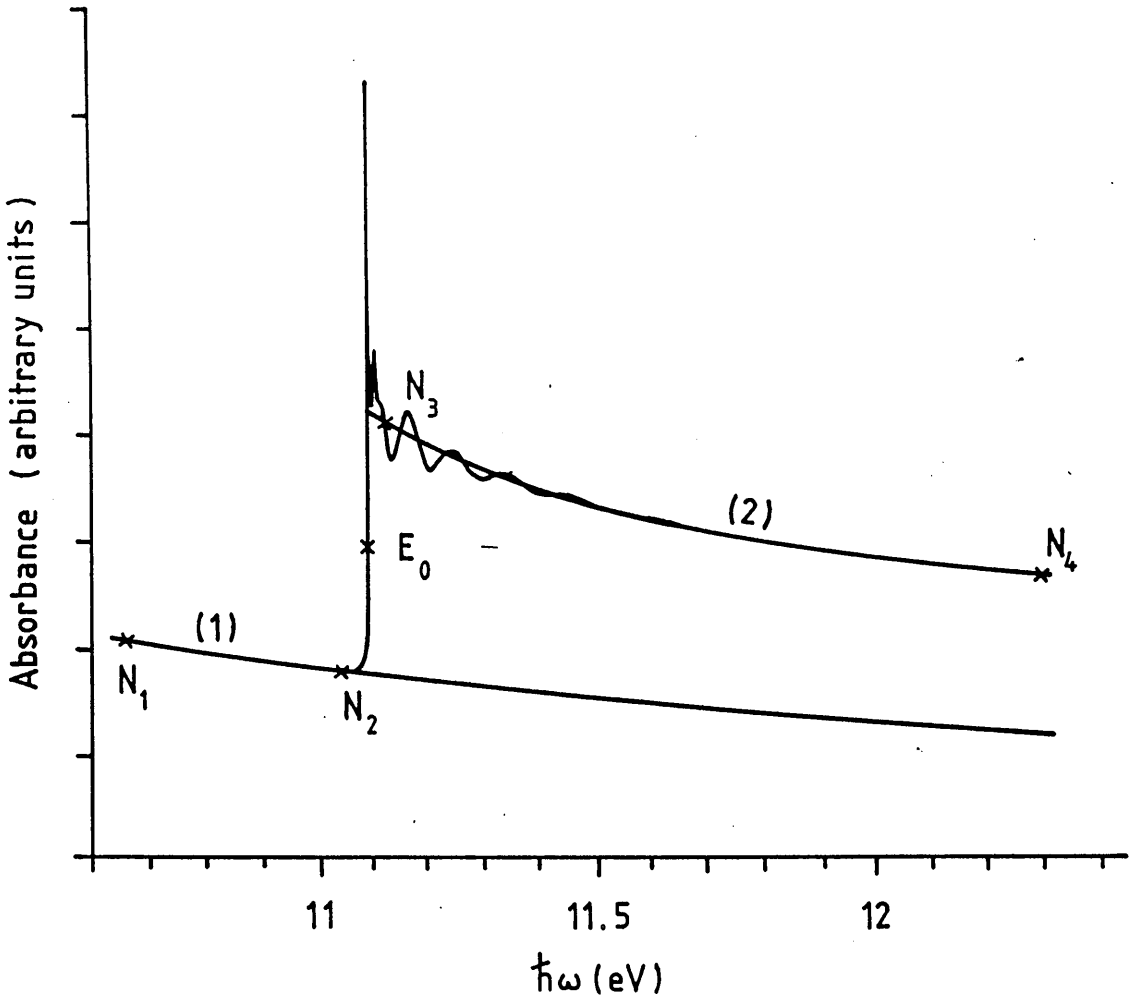


Figure 7.5

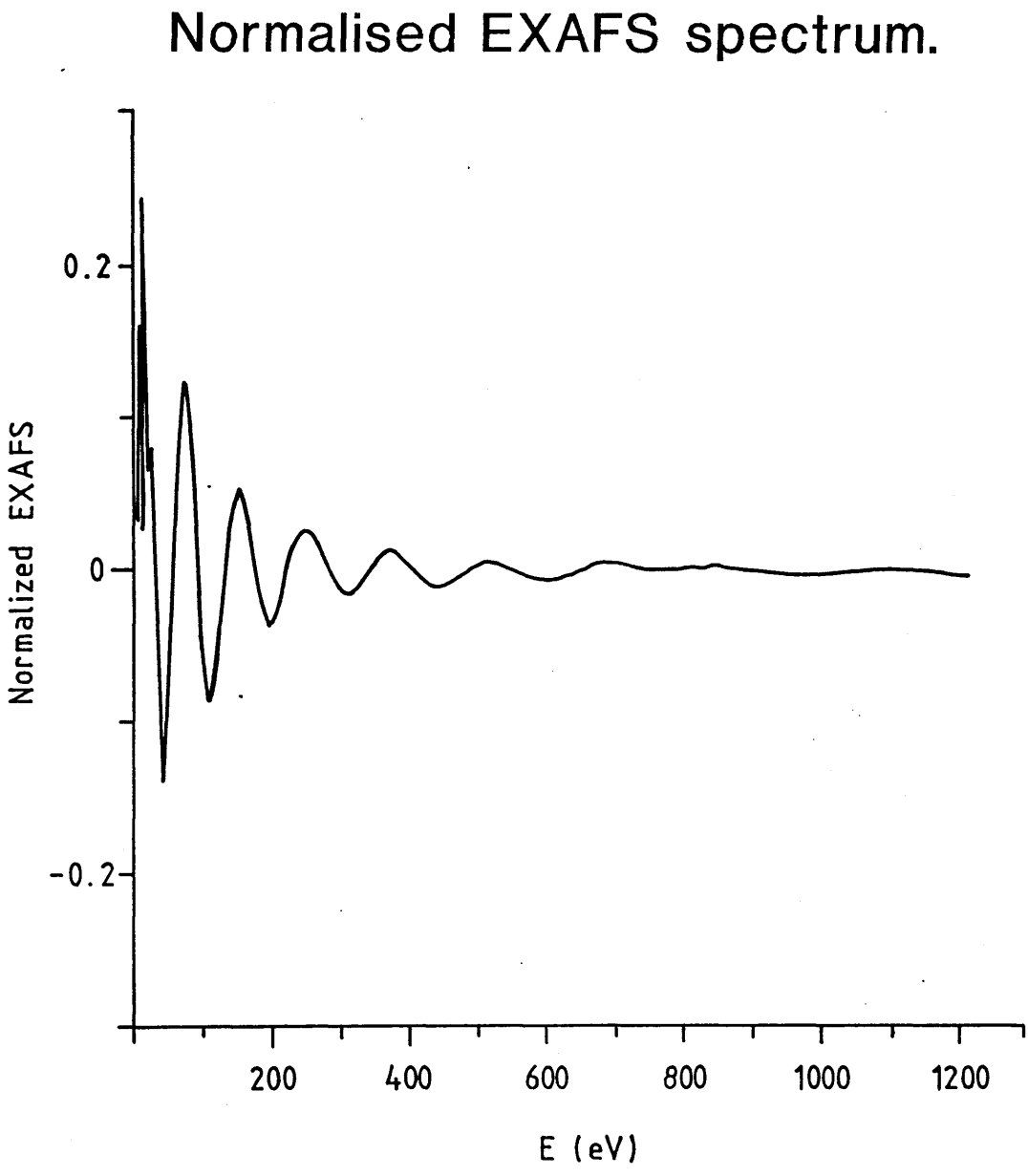

Normalised EXAFS spectrum.
0.2
0
-0.2
Normalized EXAFS
200
400
600
800
1000
1200
E (eV)

Figure 7.6

Fourier transform of EXAFS spectrum, showing peaks due to bond distances in Å.

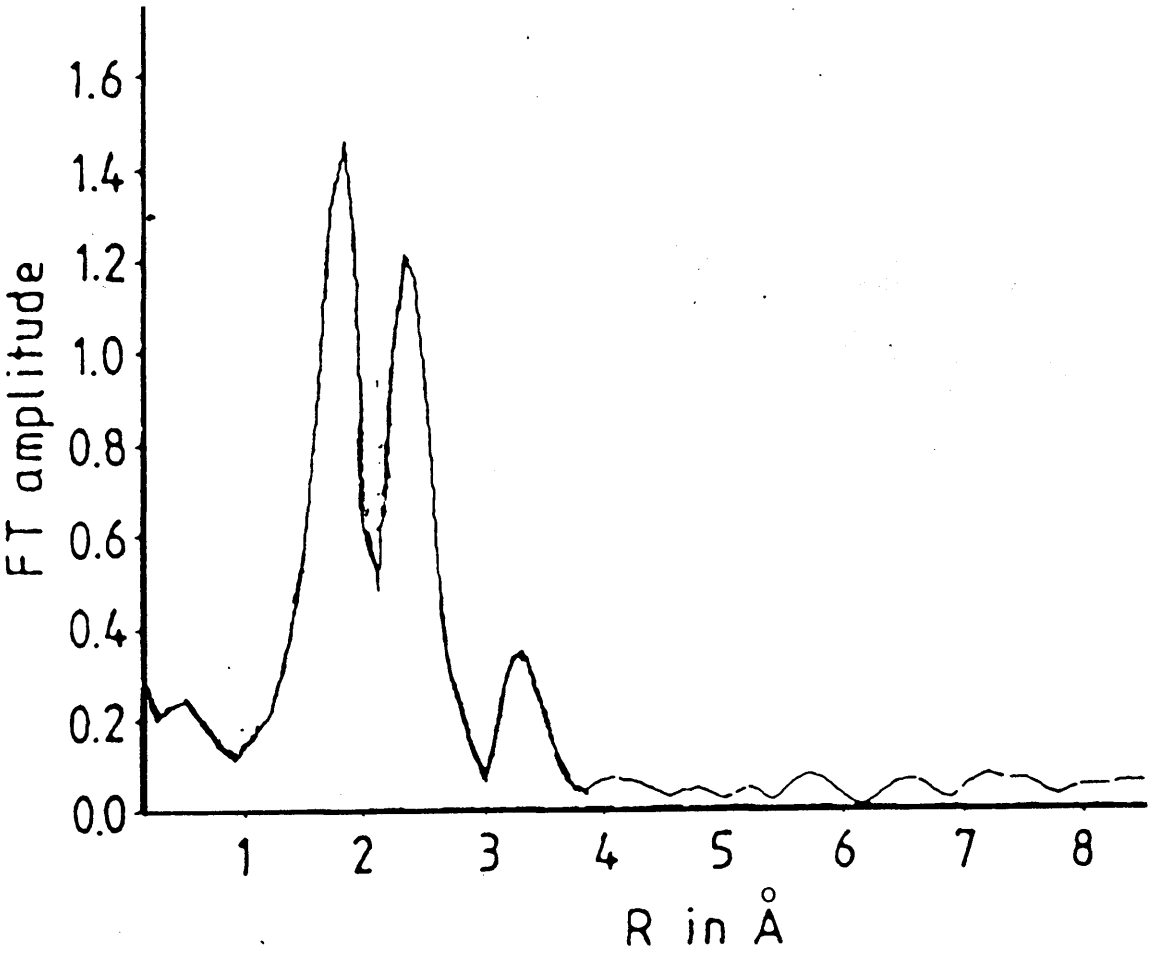


Figure 7.7

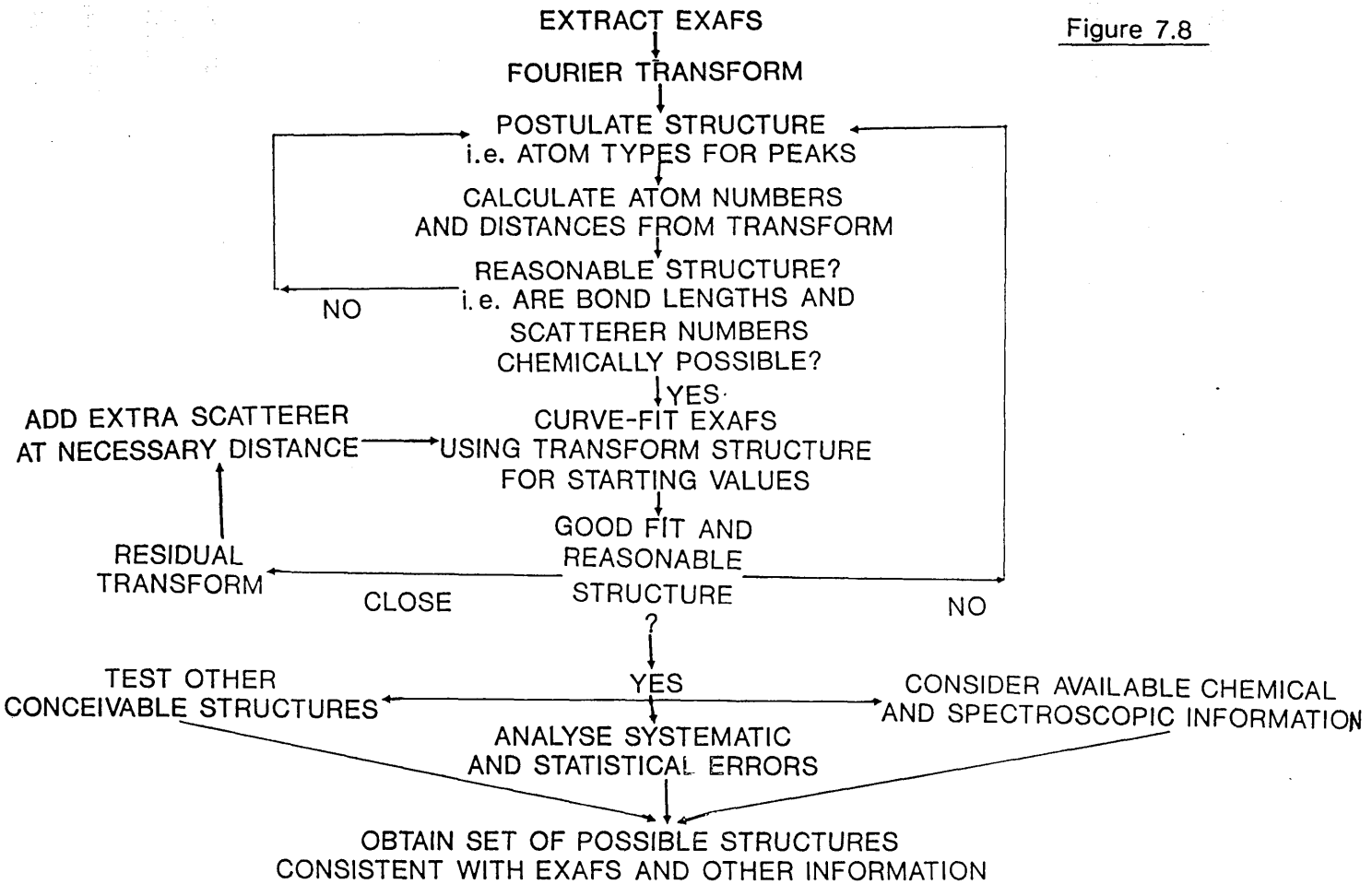

EXTRACT EXAFS
FOURIER TRANSFORM
POSTULATE STRUCTURE
i.e. ATOM TYPES FOR PEAKS
CALCULATE ATOM NUMBERS
AND DISTANCES FROM TRANSFORM
REASONABLE STRUCTURE?
i.e. ARE BOND LENGTHS AND
SCATTERER NUMBERS
CHEMICALLY POSSIBLE?
NO
YES
ADD EXTRA SCATTERER
AT NECESSARY DISTANCE
CURVE-FIT EXAFS
USING TRANSFORM STRUCTURE
FOR STARTING VALUES
GOOD FIT AND
REASONABLE
STRUCTURE
?
RESIDUAL
TRANSFORM
CLOSE
NO
YES
TEST OTHER
CONCEIVABLE STRUCTURES
CONSIDER AVAILABLE CHEMICAL
AND SPECTROSCOPIC INFORMATION
ANALYSE SYSTEMATIC
AND STATISTICAL ERRORS
OBTAIN SET OF POSSIBLE STRUCTURES
CONSISTENT WITH EXAFS AND OTHER INFORMATION

Figure 7.8

from Cramer et al[138] illustrates the complete data analysis procedure in a concise form.

Sample Preparation

Solid samples for EXAFS analysis are normally pressed between Sellotape using an aluminium spacer. Solutions are normally contained in Perspex or aluminium cells with Mylar windows. An important practical consideration in this work was the containment of chemically reactive, hydrolytically unstable samples. Cells were therefore designed so that the samples could be studied without hydrolysis. If there is too much sample, or the pathlength of the solution cell is too large, excessive X-ray absorption occurs. The windows of the cells need to be thin to minimise X-ray absorption by the window material. Glass windows can be used, so microscope slides were used in the present work. Two types of solution cell were designed, to overcome these problems, (Figure 2.1,). The aluminium cell (Fig. 2.1) consisted of a 30mm square of aluminium, 5mm wide with a recessed window giving a pathlength of 3mm. Solutions were added via Pyrex glass-to-metal seals, which were connected to the aluminium by Araldite. Mylar windows (thickness 0.07mm) were joined to the aluminium by Araldite. This gave a satisfactory seal and the cells could be evacuated to 0.05 Torr. The Pyrex cell (Fig. 2.1) was cylindrical with a diameter of 19mm and a 3mm pathlength. Microscope slides 0.15mm thick were joined to Pyrex by silicone cement. This cell could be evacuated but care had to be taken because the windows often imploded. Each cell had a

Pyrex P.T.F.E. vacuum stopcock (J. Young) fitted with a B.14 cone, the Pyrex between the stopcock and cell body acted as a storage compartment for the solution when the cell was inverted. The solution could then be kept frozen without affecting the window material. Solutions studied were prepared *in vacuo* and loaded into the cells in the glove box. The cells were then partially evacuated by expanding the gas from the cell into an evacuated manifold. The Pyrex cell (Fig. 2.1) proved the most satisfactory, and the solutions maintained their integrity over two days experimentation. The aluminium cell design was not entirely satisfactory because adhesion between the Mylar cell body and Araldite was lost at low temperature if the cell was subjected to sudden movement.

Solids were mixed with Boron Nitride using equal amounts of sample and Boron Nitride, the mixture was pressed between pieces of Mylar film (thickness 0.07mm) and an aluminium spacer (thickness 1mm). The Mylar was sealed to the aluminium using rapid setting Araldite adhesive, the spacer was made from a square of aluminium 1mm thick with 30mm sides with a window cut from the centre, dimensions 15mm x 5mm.

Nuclear Magnetic Resonance Spectroscopy [139]

Certain nuclei possess nuclear spin, and hence angular momentum P, given by

$$P = \frac{h[I(I+1)]^{\frac{1}{2}}}{2\pi} \qquad 2$$

I is the spin quantum number. In Inorganic chemistry many nuclei of interest have $I = \frac{1}{2}$, which is very useful since for a number of reasons, it is generally easier experimentally to observe NMR signals from these nuclei. The angular momentum gives rise to a nuclear magnetic moment, μ related directly by

$$\mu = \zeta P \qquad 3$$

The constant of proportionality ζ is the magnetogyric ratio and is an important property of the nucleus. The nuclear magnetic moment, μ, is quantised, and in a magnetic field, Bo, these quantised levels are no longer degenerate. For $I = \frac{1}{2}$ nuclei there are $(2I + 1)$ i.e. 2 energy levels, corresponding to the nuclear spin being either parallel ($M_1 = \frac{1}{2}$) or antiparallel ($M_1 = -\frac{1}{2}$) to the magnetic field. An experiment consists of inducing transitions between these non-degenerate energy levels by radio-frequency electromagnetic energy.

NMR spectroscopy can provide extremely useful information about the chemical environment of the different nuclei in a compound, and has become one of the most powerful tools available for structural analysis. An important problem in measuring most nuclei of interest is that it can be very difficult to detect the transitions between nuclear spin levels because their transitions

are so weak. The frequency ν of the electromagnetic radiation causing transitions between nuclear levels is given by

$$\nu = \frac{\zeta \, Bo}{2\pi} \qquad 4$$

Where Bo is the applied magnetic field. An increase in Bo leads directly to an increase in the frequency of the NMR transition. Even for the strongest available magnetic fields this frequency is very low, in the radio frequency range of the electromagnetic spectrum. Due to the Boltzmann distribution, there is only a slight difference in the populations of the energy levels. Because the NMR transitions depend on the population difference, the strengths of some NMR signals are very weak compared with, infrared or UV-visible spectroscopy, where there are large differences in populations between the relevant energy levels. The traditional method of obtaining NMR spectra consists of altering the wavelength of the electromagnetic radiation supplied and observing the absorption. This is called continuous wave (CW) spectroscopy. However this method is only feasible for nuclei such as ^{1}H and ^{19}F which produce relatively strong NMR signals, and even then quite concentrated solutions are needed. The magnetogyric ratio ζ directly determines the frequency of the NMR transitions of a particular nucleus. The receptivity of a particular nucleus depends on ζ and the natural abundance. For example the proton (^{1}H) is set at a standard 1.0. The carbon NMR isotope ^{13}C has $I = \frac{1}{2}$ and has a natural abundance of only 1.1%. Because of this low abundance, and also the smaller ζ value, its relative receptivity is 1.76×10^{-4} compared with the proton. For this reason the

continuous wave method is not used when measuring ^{13}C spectra. The CW method would require ^{13}C isotopically enriched samples with a high carbon content. The former is very expensive and the latter not always possible to achieve in practice. Pulsed NMR is therefore used for ^{13}C spectra and many other nuclei of low receptivity. It is possible to apply electromagnetic radiation energy effectively over the whole range of the spectrum in a short, intense pulse and to observe the spectral effect produced by the nuclei promoted to their upper energy state as they fall back to the lower energy state. The record thus obtained (free induction decay) FID is not identical to the normal absorption spectrum but is related to it and may be converted by performing a Fourier Transform. In the present work ^{1}H, ^{13}C, ^{19}F and ^{125}Te F.T. NMR spectroscopy were employed to identify products of reactions.

Sample Preparation.

Samples for NMR spectroscopy were prepared in single limbed Pyrex vessels fitted with 5mm precision NMR tubes. The tubes were sealed under vacuo using a gas/oxygen flame. Generally [^{2}H]-hydrogen labelled acetonitrile was used as a solvent and propionitrile was added when necessary for low temperature work. Liquid SO_2 was used as a solvent for some of the ^{125}Te spectra. Spectra were recorded at various temperatures, in order to try and surpress exchange between co-ordinated and uncoordinated solvent, and rapid fluoride ion exchange, which occurred in some spectra. Spectra were obtained using a Bruker WP200JY spectrometer.

Mass Spectroscopy [140]

A mass spectrometer is an instrument that converts a molecule into positive ions and then separates the ions as a function of mass/charge ratio. It also displays the relative abundances of the ions formed. The sample is converted to the gas phase and is ionised by collision with a high energy electron beam. The ion fragments are accelerated by an electric field gradient, so that they enter the mass analyser with a high velocity. The behaviour of the fragments in the magnetic field is the basis of mass/charge separation. At a particular energy only certain ions will follow the path to the detector, due to the correct balance of momentum versus magnetic field deflection. The mass spectrum may be scanned by varying either the accelerating potential (V) or the applied field strength (H).

In the electric field the potential energy PE (eV) of an ion is equal to its Kinetic energy KE when acceleration is complete giving

$$eV = \tfrac{1}{2} mv^2 \qquad 5$$

where e = electrical charge

V = acceleration potential

m = ion mass

v = ion velocity

In a magnetic field the ion is subjected to two forces in equilibrium, the centrifugal force $\frac{mv^2}{R}$ and the centripetal Hev

where H = the magnetic field intensity

R = Radius of influence of field.

$$Hev = \frac{mv^2}{R} \qquad 6$$

combining (5) and (6) and rearranging gives

$$\frac{m}{e} = \frac{H^2R^2}{2V} \qquad 7$$

From (7) it can be seen that by scanning the magnetic field, the equation can be satisfied for ions of all m/e ratios for fixed values r and V. Alternatively the mass spectrum may be scanned by varying V while the magnetic field is held constant. Mass spectrometry is therefore a very useful technique for determining molecular formulae or functional groups.

In this work mass spectrometry proved useful in identifying products from bromination reactions. Bromine has two stable isotopes ^{79}Br and ^{81}Br their natural abundances are 50.54 and 49.46% respectively; this aids the interpretation of mass spectra containing bromine. Two peaks of nearly equal intensity will occur for each fragment containing bromine. In a molecule containing two bromine atoms, three lines with ratios of 1:2:1 would result from different combinations of isotopes in a fragment containing two bromine atoms, all peaks would be 2 mass units apart.

This was useful in the present work, when assigning polybrominated organic products.

Vibrational Spectroscopy[141,142]

Infrared and Raman spectroscopy were used to help identify the complexes synthesised during this project. They were most useful in detecting the presence of coordinated ligands, and the presence of fluoroanions. Due to the hygroscopic nature of the compounds studied, sample preparations for infrared and Raman were non routine. Infrared samples were made using sodium dried Nujol or Fluorolube as mulling agents in the glove box. The spectra were recorded as soon as possible after removing from the inert atmosphere. This technique has the disadvantage that hydrolysis may occur when grinding, from the Nujol, or from the infrared windows. Assignment of bands is therefore always better supported by Raman data, the two techniques complementing each other.

Raman spectra can be obtained in well flamed out Pyrex capillaries, which minimises hydrolysis. The technique is non-destructive so samples can be used for other analytical procedures. Raman solution studies can easily be undertaken, and certain bands can be polarised in solution. When a band is polarised completely, this indicates the vibration is A_{1g}, in O_h totally symmetric, which is ν_1 of an octahedral molecule such as the hexafluoroanions studied in this work. One of the disadvantages of Raman spectroscopy is that fluorides are generally poor Raman scatterers, so spectra are sometimes difficult to obtain. Samples can easily be decomposed by the laser beam, this can be prevented in some instances by changing the laser frequency, by cooling, or by spinning the sample. Raman spectra of solutions can be studied in <u>situ</u>, that is by shining the laser beam through the Pyrex reaction vessel; this enables concentrations of reactants

to be varied and the growth or disappearance of a band monitored.

The energies of most molecular vibrations correspond to those of the infrared region of the electromagnetic spectrum. By measuring these energies it is possible to assign molecular vibrations occurring in an infrared spectrum or indirectly in a Raman spectrum. Vibrational modes of a molecule are excited by the absorption of quanta whose energies lie in the infrared region of the electromagnetic spectrum. The vibrational transitions are also detected by Raman scattering. A molecular vibration is infrared active if there is a change in dipole during vibration; in the Raman effect a molecule scatters the monochromatic radiation of frequencies that are shifted to higher or lower wavenumbers with respect to the exciting frequency. These shifts (Raman lines) are produced if the molecule vibrates in such a way that its polarisability is changed during the vibration. The mutual exclusion rule for a polyatomic molecule having a centre of symmetry states that the vibrations symmetric with respect to the centre of symmetry are Raman active, but infrared inactive, and the vibrations antisymmetric with respect to the centre of symmetry are infrared active but Raman inactive.

Sample Preparation

Samples were ground in the glove box using an agate mortar and pestle. Nujol (liquid paraffin) or Fluorolube (a fluorocarbon oil) was added forming a homogeneous paste, this was smeared evenly between silver chloride or silicon plates, which were then mounted in a suitable holder. Gas infrared spectra were recorded using

a Pyrex gas cell (path length 5cm) fitted with silver chloride windows joined to the Pyrex using silicone sealant (R.S. Components) or Araldite adhesive. Spectra were recorded over the range 4000 - 400 (AgCl windows) or 4000 - 200 cm^{-1} (silicon windows) respectively using Perkin Elmer 580 or 983 spectrophotometers with a 3600 data station interfaced to the latter. Raman spectra of solids and solutions were recorded in Pyrex capillaries sealed in vacuo. Spectra were recorded using a Spex Ramalog spectrometer using Krypton or Argon ion lasers, producing excitation frequencies of 647.1, 514.5 and 488.0 nm.

Electronic Absorption Spectroscopy [143]

Electronic spectroscopy involves the study of the transitions of an electron in a molecule or in a metal ion. Electronic transitions occur after absorption of U.V. visible or near infrared radiation. There are certain selection rules which are relevant to electronic spectroscopy. If the transition causes the number of unpaired electrons to change in going from ground state to excited state, these are referred to as "spin" or "multiplicity" forbidden. If the transitions involve redistribution of electrons in a given set of orbitals these are "Laporte" forbidden. Due to this Laporte rule, pure d-d transitions are forbidden so many transition metal complexes should be colourless, except for the following consideration. If a transition metal ion does not have a centre of symmetry or vibrates causing the symmetry to be destroyed, mixing of orbitals can occur, for example p and d, and the transition occurs between d levels with different amounts of p character.

When an octahedral molecule with O_h symmetry is vibrating normally, the molecules distort from pure O_h symmetry. This causes the d and p orbitals to mix in the non-centrosymmetrical configuration and a very low intensity transition is observed (ε = 5 to 25 $dm^3\ mol^{-1}\ cm^{-1}$). The transitions are vibronically allowed and the phenomenon is described as vibronic coupling. This is important in metal ions with unfilled d or f shells, such as MoF_6^- ($4d^1$), WF_6^- ($5d^1$) or UF_6^- ($5f^1$). In the present work uranium(V) compounds were identified from their near infrared-visible electronic spectra. The f-f transitions involved are weaker than d-d transitions but consist of fairly sharp groups of lines corresponding to transitions between

the ground state and the upper Stark levels of the ions.[84] Chapter 5, Figure 5.2 shows electronic spectra due to UF_6^- and UF_5, these spectra were useful in identifying the presence of the UF_6^- anion or UF_5NCMe, which is a product from solvent attack when UF_6 is in contact with MeCN for a long time. Uranium(V) chloride fluorides have recently been prepared[106,108] and identified by their electronic spectra. These spectra enabled the reaction of chlorine or HCl with UF_6 in acetonitrile to be followed by electronic spectroscopy.

Oxidation of tellurium using various high oxidation state fluorides was followed with electronic spectroscopy. The Te cations formed gave coloured solutions in the visible region, which could be assigned by comparison with literature spectra.

The oxidation of iodine by Br^+ was studied using electronic spectroscopy. The band at 460 nm due to I_2 in MeCN decreased by adding $[Br(C_3H_9N_3)][UF_6]$; this provided evidence for the Br^+ cation being monopositive, with the above empirical formula.

Sample Preparation

A Pyrex vessel equipped with a 10mm Spectrosil cell was used for recording solution spectra. The compounds were loaded into the cell in the glove box and MeCN was distilled in under vacuum. The solution was decanted into the Spectrosil cell and the spectrum recorded using a matching cell with MeCN as a reference. All spectra were recorded on Beckman 5270 or Perkin Elmer Lambda 9 spectrometers over the range 1600 - 200 nm.

Conclusions and Future Work.

The EXAFS study provided structural evidence for the existence of the linear centrosymmetric $I(NCMe)_2^+$ cation in the solid state and in MeCN solution. Subsequent substitution reactions studied by others in this department, where the MeCN ligands were replaced by other species such as dimethyl sulphide (Me_2S), trimethylthiourea (tmtu) and N_4 - nitrogen macrocycles, showed there were analogies between iodine(I) and metal cation coordination chemistry. The oxidation of bromine by UF_6 in MeCN provided a second type of cationic species. The cation $Br(C_6H_9N_3)^+$ was a good oxidising agent and it halogenated aromatic compounds in a similar manner to that of the iodine cation. Future work can include trying to synthesize new reagents which incorporate electrophilic bromine supported on inorganic materials and to study their reactions under heterogeneous conditions.

Chlorine was not oxidised to a simple cationic species, however, UF_6 was reduced to UF_5.NCMe in the presence of Cl_2 in MeCN and substitution reactions did occur to give $UF_{5-x}Cl_x$.NCMe species.

Tellurium was oxidised using several oxidising agents, this could lead to analogous research into the oxidation of other group VI and group V elements. The cationic species formed could provide new reagents which may be useful in electrophilic reactions. Macrocyclic N-4 donor ligands could be used to stabilise the high oxidation state and the macrocyclic cation could be supported on inorganic oxides of high surface area.

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